Electronic Supplementary Material (ESI) for CrystEngComm.

ELECTRONIC SUPPLEMENTARY INFORMATION FILE

CXXX CARBAMATES (X = F, Cl, Br)

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CxxF

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CxxCl

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CxxBr

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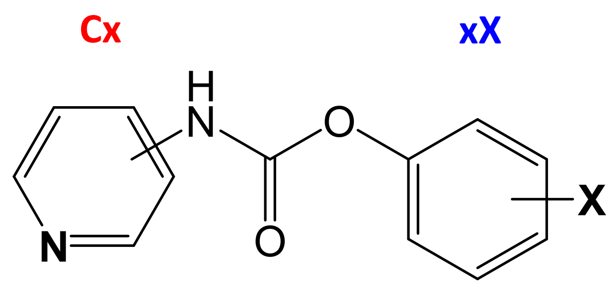


CxxX series with **X** = **F**, **Cl**, **Br**

Schematic diagram of the **CxxX** series of isomers (with **Cx** as the aminopyridine group and **xX** as the halophenyl moiety). The series represents the 3 × [3 × 3] isomer grids comprising 27 mono-halogenated carbamate compounds. The methyl (isomer grid) series is represented by **CxxM** (**M** for CH_3)[8c] and the methoxy series is **CxxOMe** (OMe = methoxy)[8a] and both the methyl and methoxy are positioned on the phenyl ring in a similar fashion to **CxxX**.

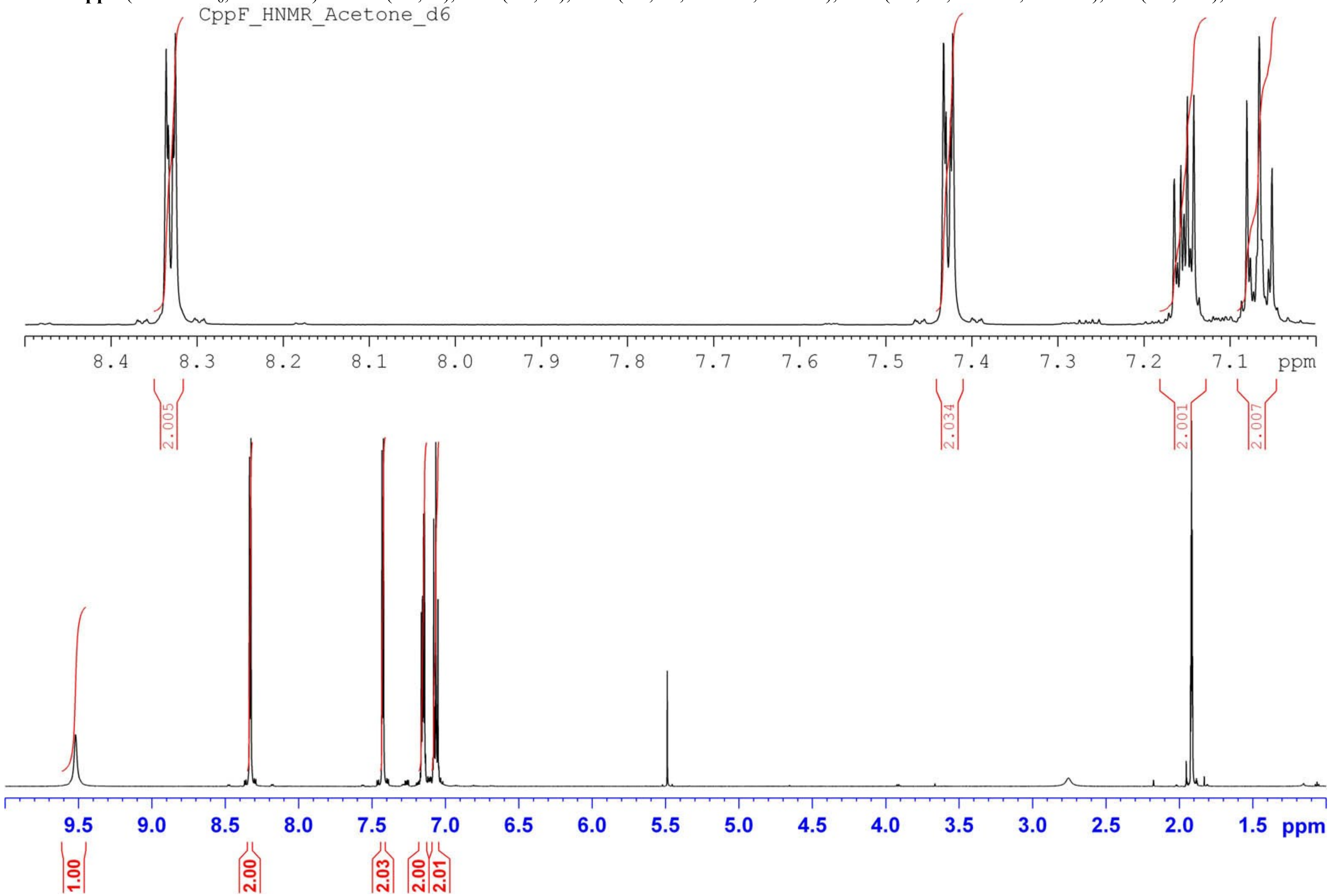
1.1. The CxxF isomer grid

^{1}H NMR data	**Pages 3-16.**	(run in CD_3COCD_3, acetone-d_6 and $CDCl_3$, deuterated chloroform)
^{13}C NMR data	**Pages 17-23.**	
^{19}F NMR data	**Pages 24-30.**	
Infra-red data	**Pages 31-37.**	

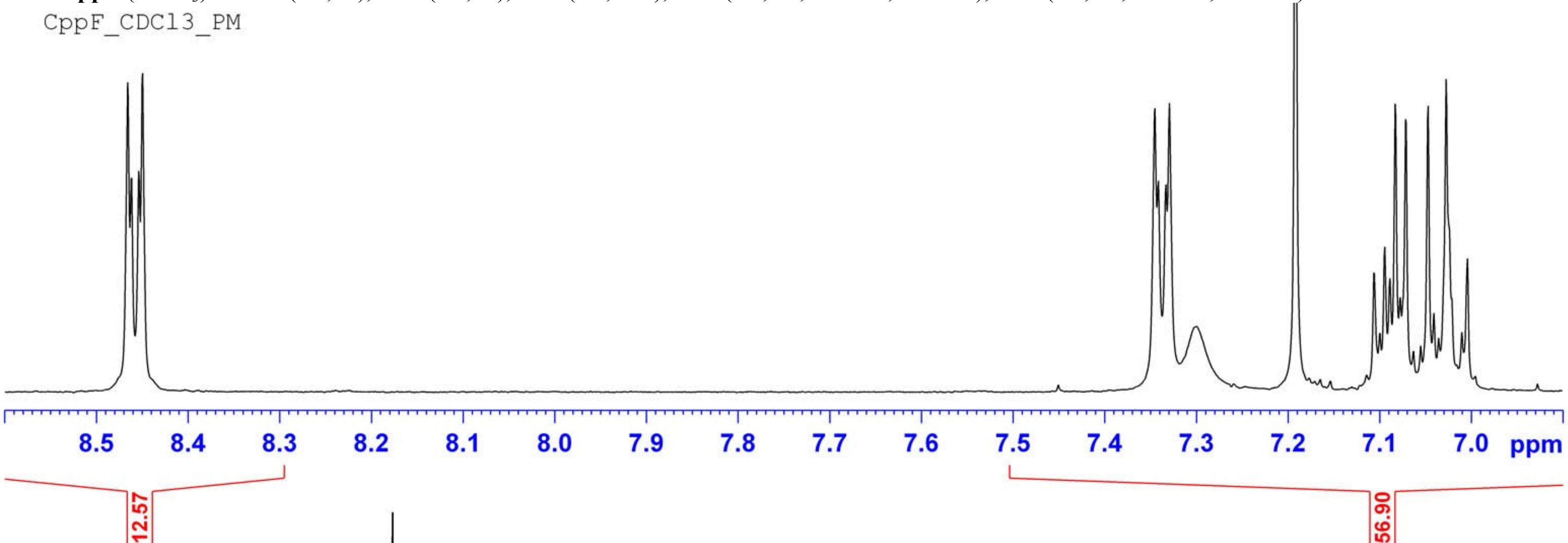
Note: The ^{1}H NMR data for all 24 synthesised **CxxX** compounds were analysed in CD_3COCD_3, acetone-d_6 and $CDCl_3$, deuterated chloroform. It has been noted that for several **CxxX** compounds (*i.e*. **CpoF**, **CmoF**, **CpmCl**, **CpoCl**, **CooCl**, **CpmBr** and **CpoBr**) that the aromatic C-H were observed as overlapping multiplets and often coincidental with residual $CHCl_3$ solvent (when run in $CDCl_3$). The acetone (CD_3COCD_3) spectra often provided an alternative and cleaner looking spectrum in terms of overlapping aromatic multiplets and solvent peaks in the aromatic region.

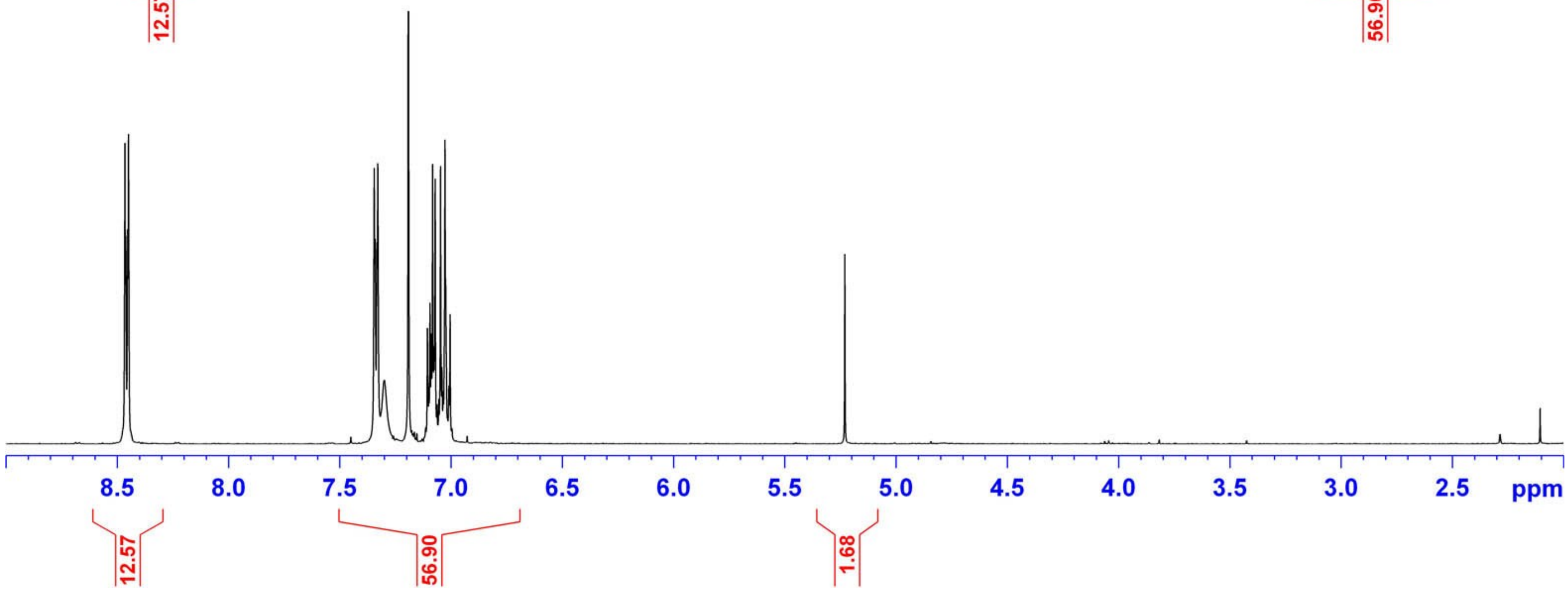
^{1}H NMR data and spectra (400 MHz)

1.1.1.1. **CppF** (Acetone-d_6, 600 MHz): δ 7.07 (2H, m), 7.15 (2H, m), 7.34 (2H, dd, ^3J = 4.9, ^4J = 1.5), 8.33 (2H, dd, ^3J = 4.8, ^4J = 1.5), 9.5 (1H, br s);

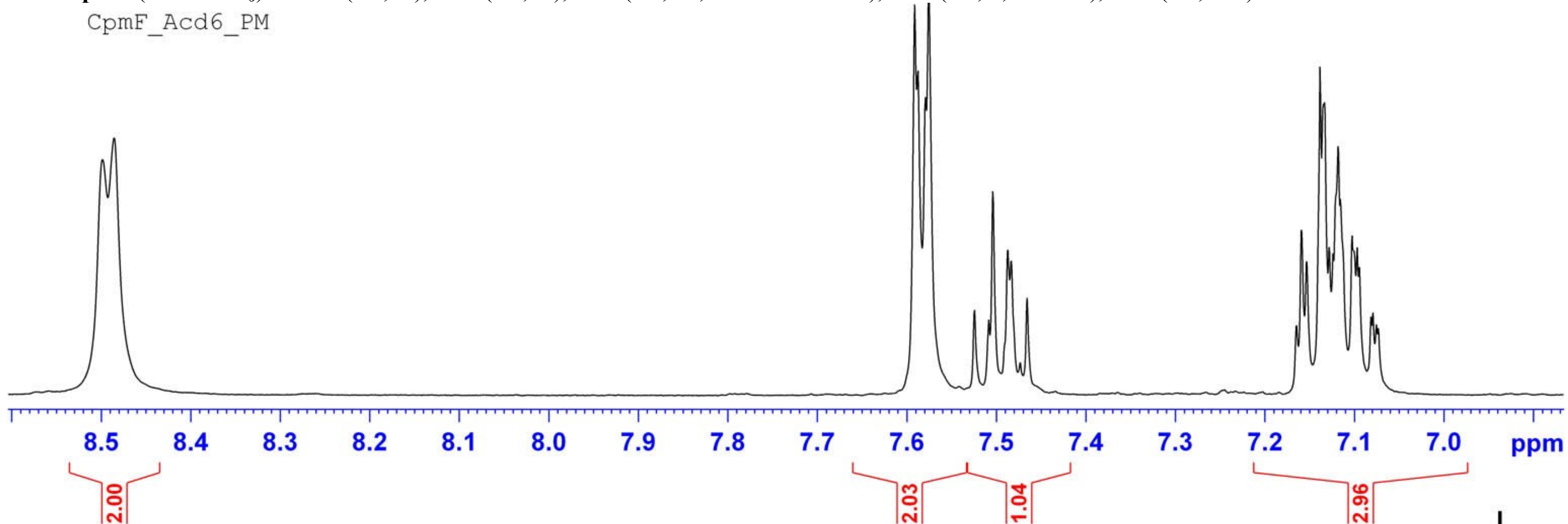


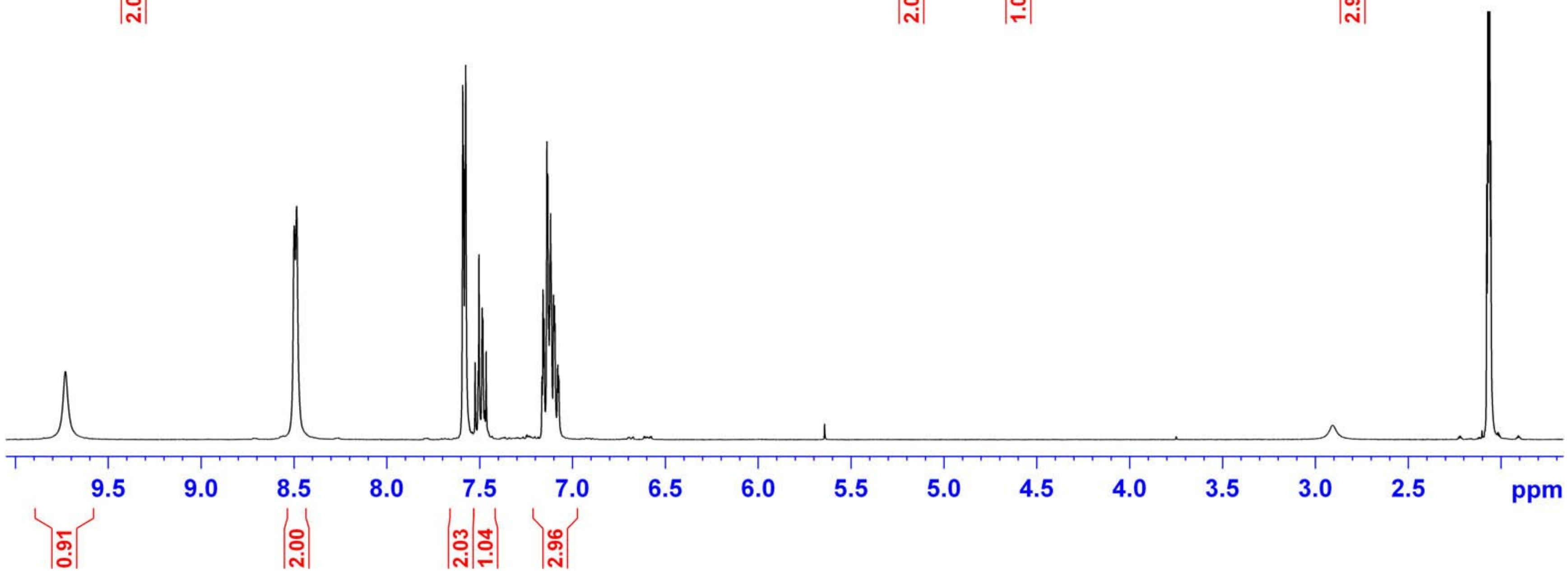
1.1.1.2. **CppF** ($CDCl_3$) δ 7.03 (2H, m), 7.09 (2H, m), 7.30 (1H, br s), 7.34 (2H, dd, ^3J = 4.5, ^4J = 1.5), 8.46 (2H, dd, ^3J = 4.8, ^4J = 1.5)



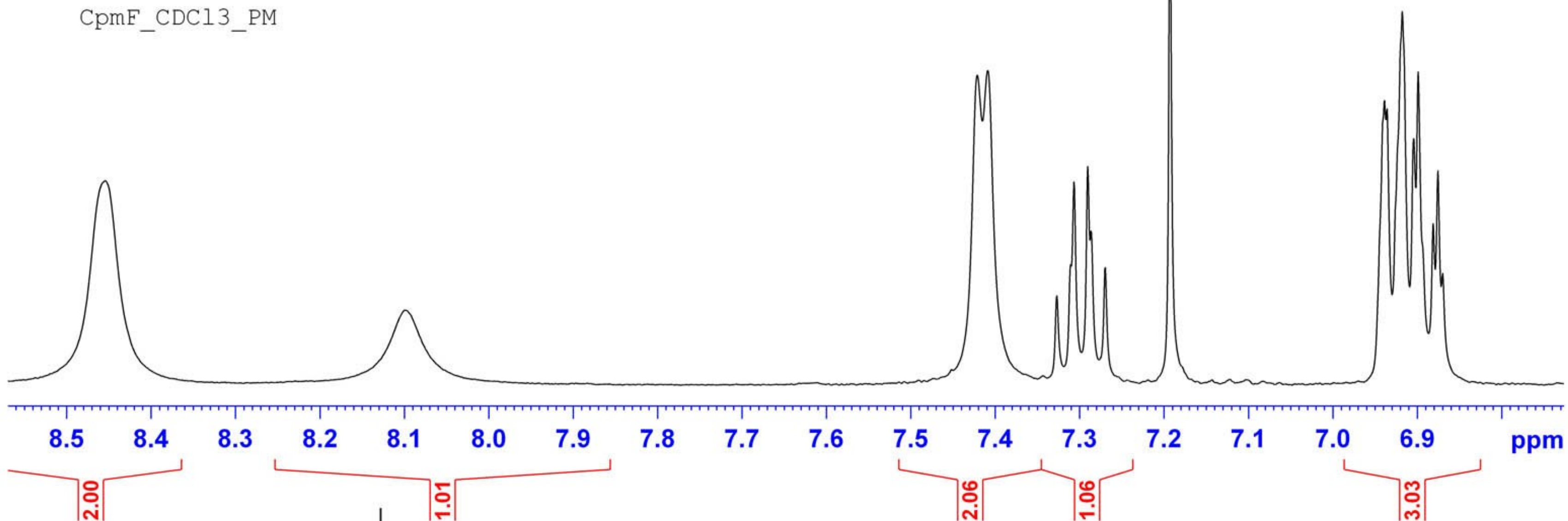


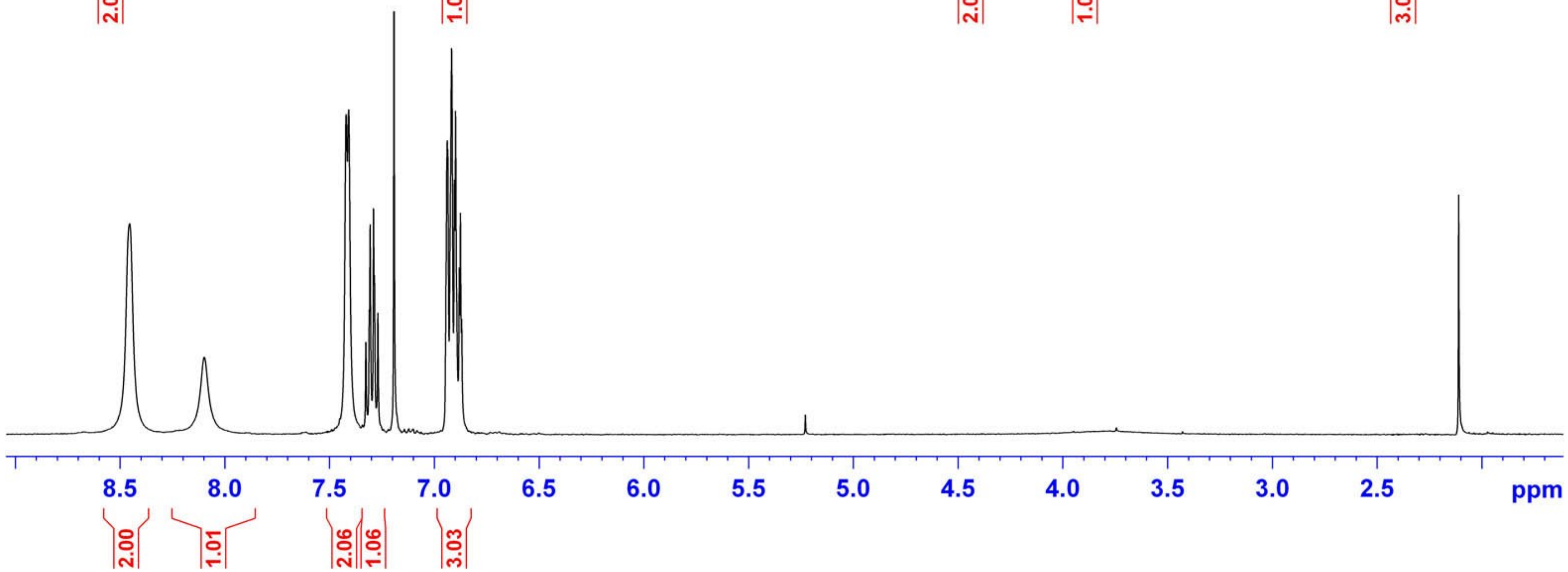
1.1.1.3. **CpmF** (Acetone-d_6): δ 7.12 (3H, m), 7.49 (1H, m), 7.58 (2H, dd, ^3J = 4.5 ^4J = 1.5), 8.49 (2H, d, ^3J = 5.2), 9.73 (1H, br s)



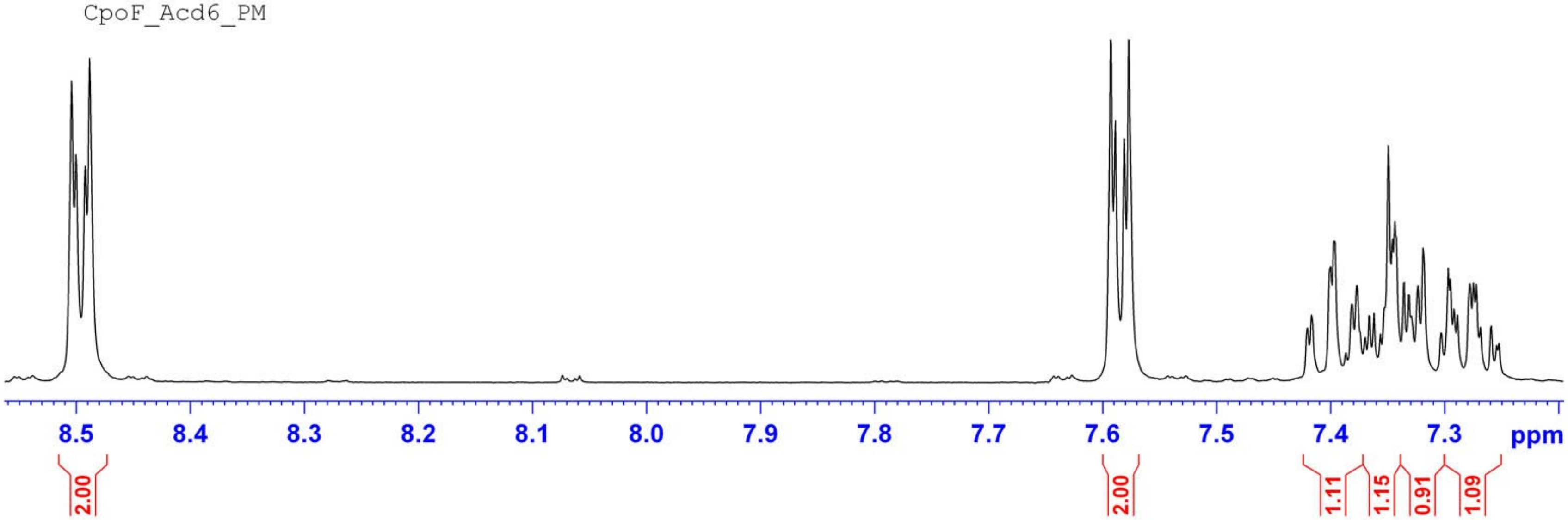


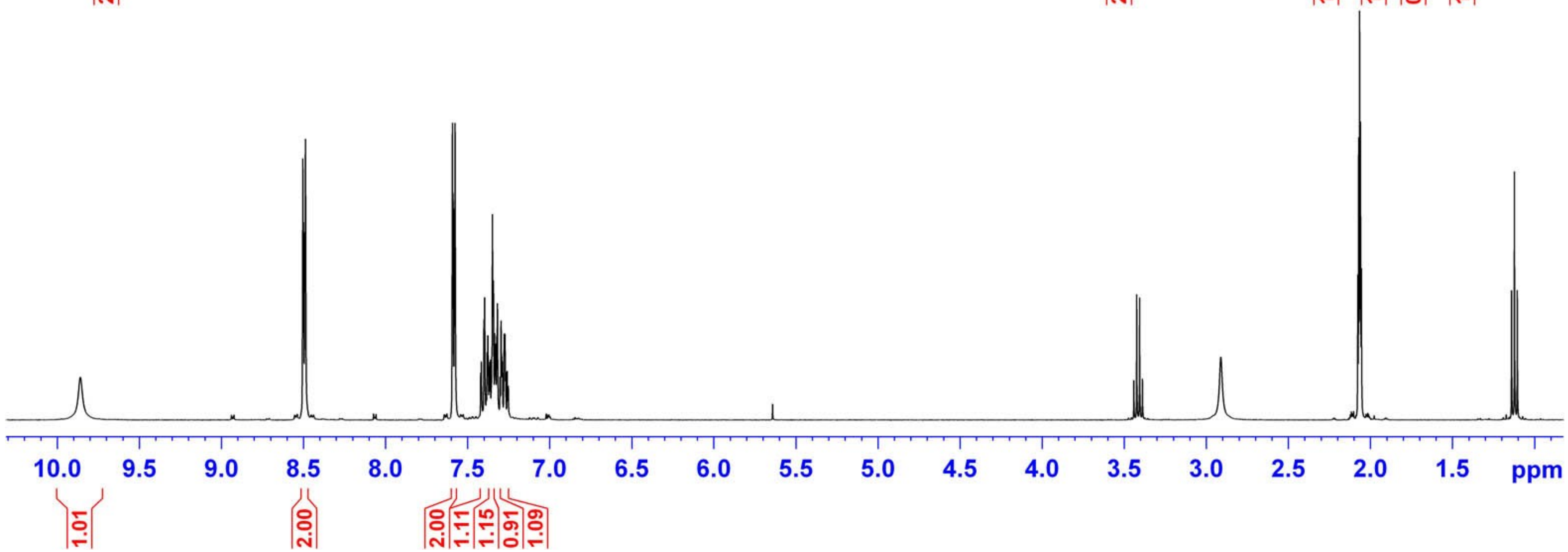
1.1.1.4. **CpmF** ($CDCl_3$) δ 6.91 (3H, m), 7.30 (1H, td, ${}^3J$ = 8.5 ${}^4J$ = 6.6), 7.41 (2H, d, ${}^3J$ = 4.9), 8.10 (1H, br s), 8.45 (2H, s);



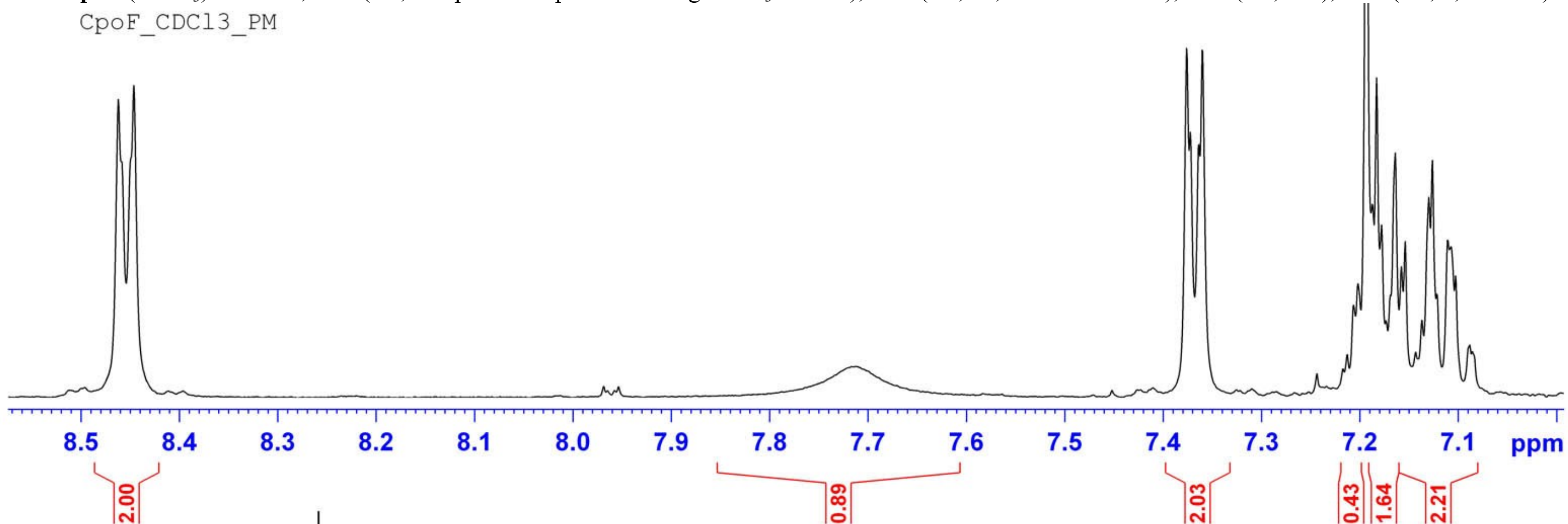


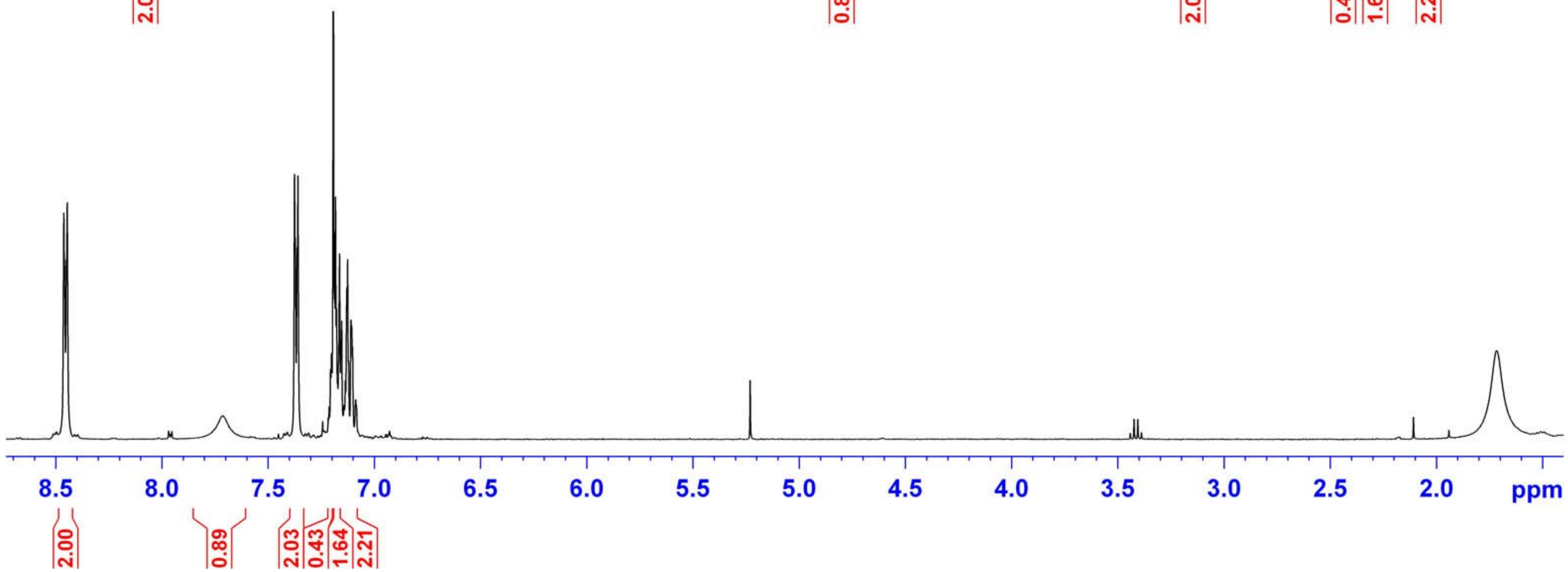
1.1.1.5. **CpoF** (Acetone-d_6): δ 7.33 (4H, m), 7.58 (2H, dd, ^3J = 4.9 ^4J = 1.6), 8.5 (2H, dd, ^3J = 5.1 ^4J = 1.5), 9.86 (1H, br s)



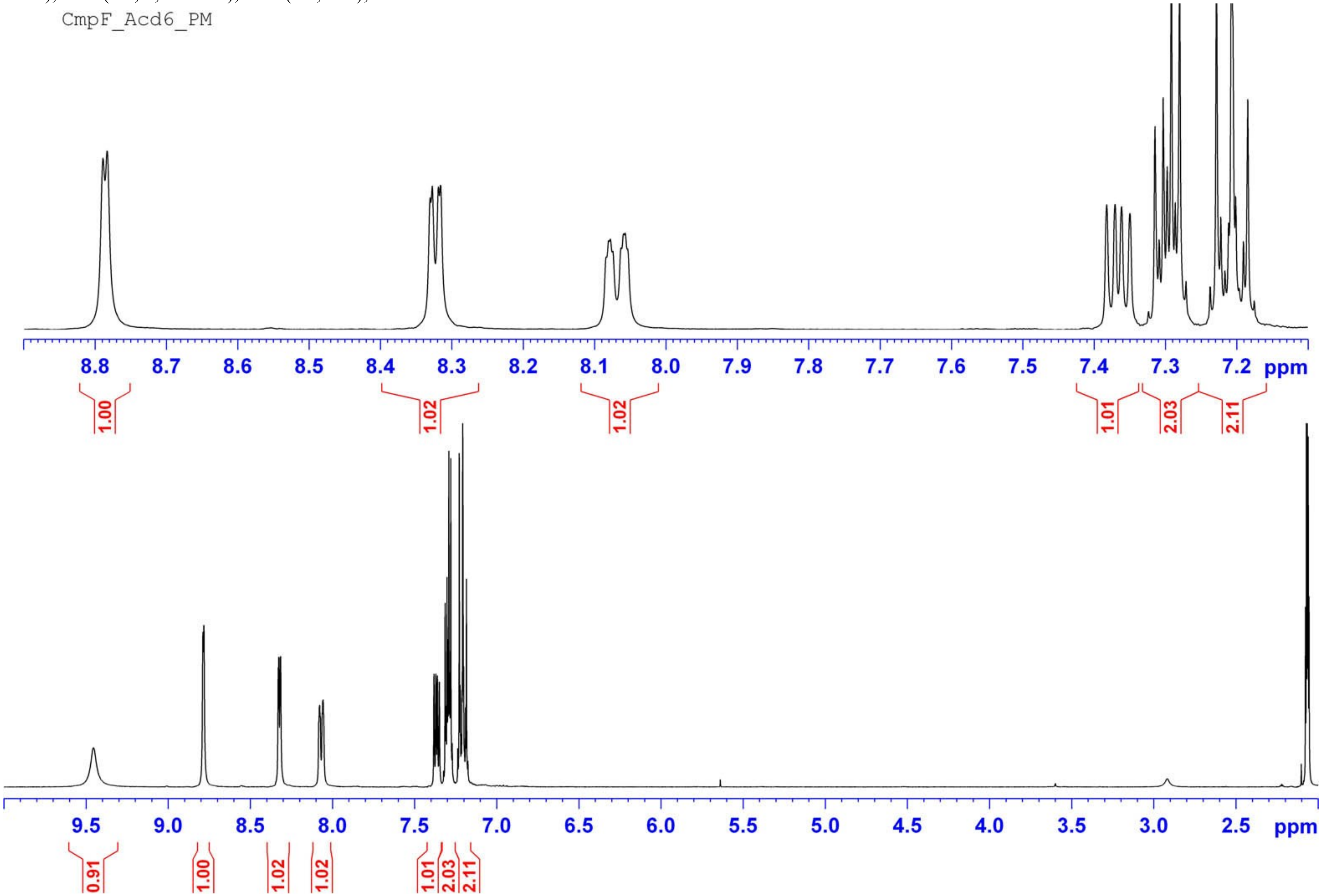


1.1.1.6. **CpoF** ($CDCl_3$) δ at 7.11, 7.17 (4H, complex multiplets including $CHCl_3$ solvent), 7.37 (2H, dd, ^{3}J = 5.1 ^{4}J = 1.5), 7.71 (1H, br s), 8.45 (2H, d, ^{3}J = 4.9)

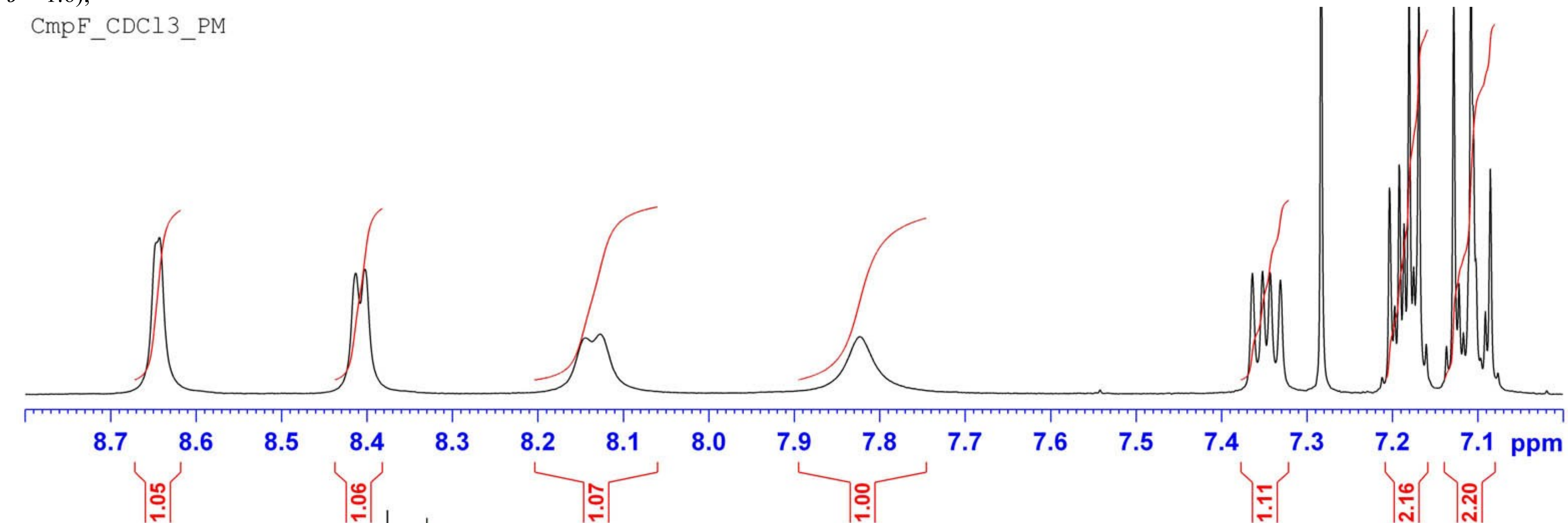


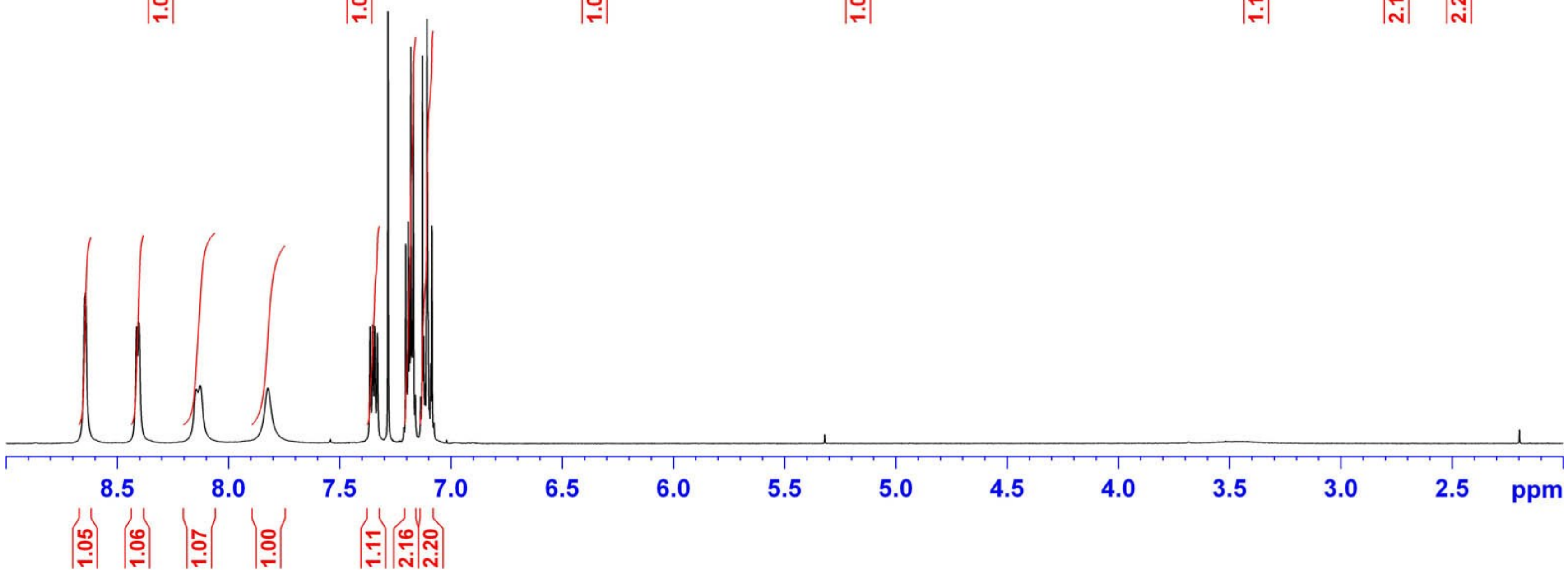


1.1.1.7. **CmpF** (Acetone-d6): δ 7.21 (2H, m), 7.29 (2H, m), 7.37 (1H, dd, ^{3}J = 8.3, ^{4}J = 4.7), 8.07 (1H, ddd, ^{3}J = 8.4, ^{4}J = 2.9, ^{5}J = 1.3), 8.32 (1H, dd, ^{3}J = 4.8, ^{4}J = 1.3), 8.78 (1H, d, ^{3}J = 2.3), 9.45 (1H, br s);

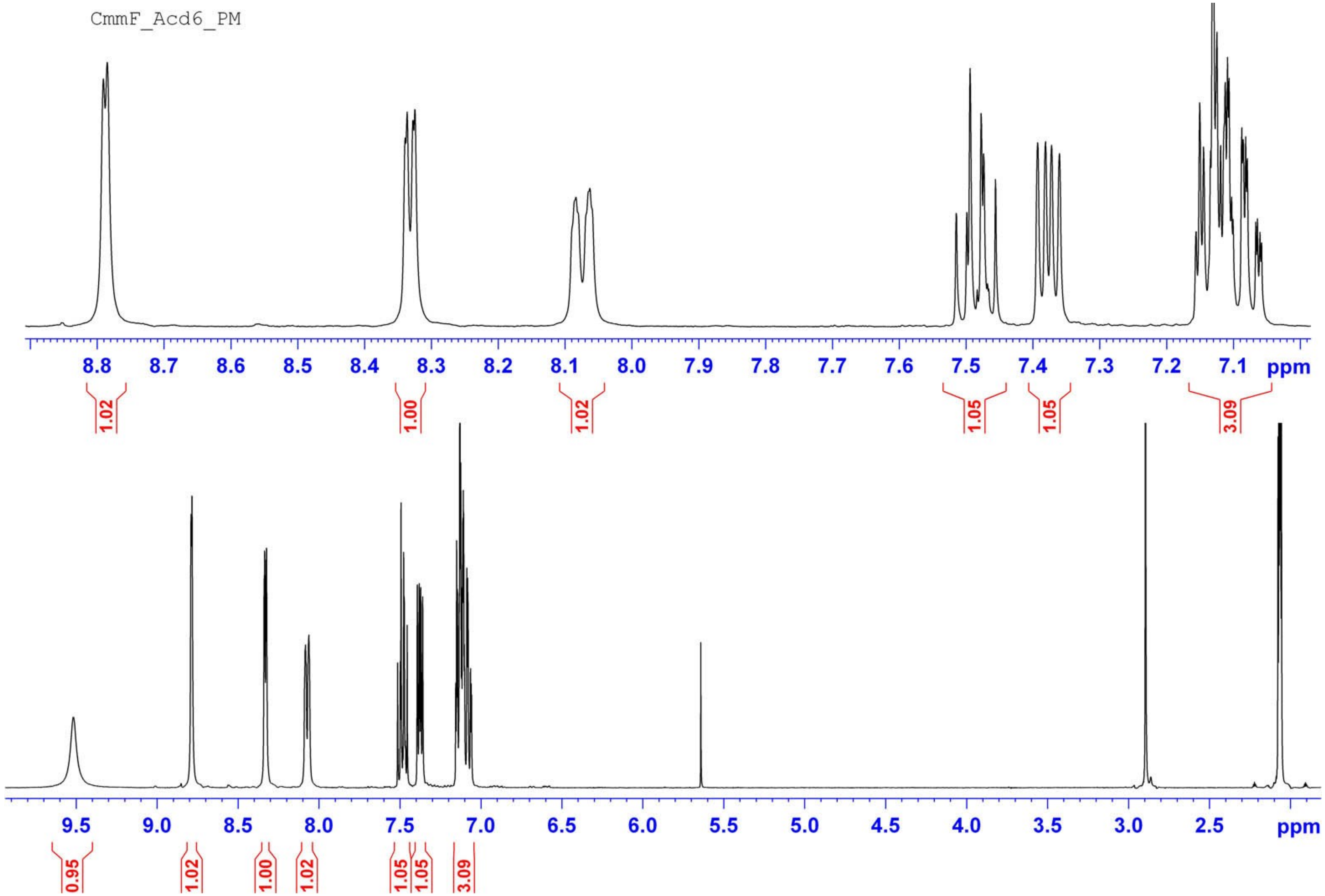


1.1.1.8. **CmpF** ($CDCl_3$) δ 7.11 (2H, m), 7.18 (2H, m), 7.35 (1H, dd, ^3J = 8.5, ^4J = 4.8), 7.82, (1H, br s), 8.14 (1H, d, ^3J = 7.2), 8.41 (1H, d, ^3J = 4.4), 8.64 (1H, d, ^3J = 1.6);

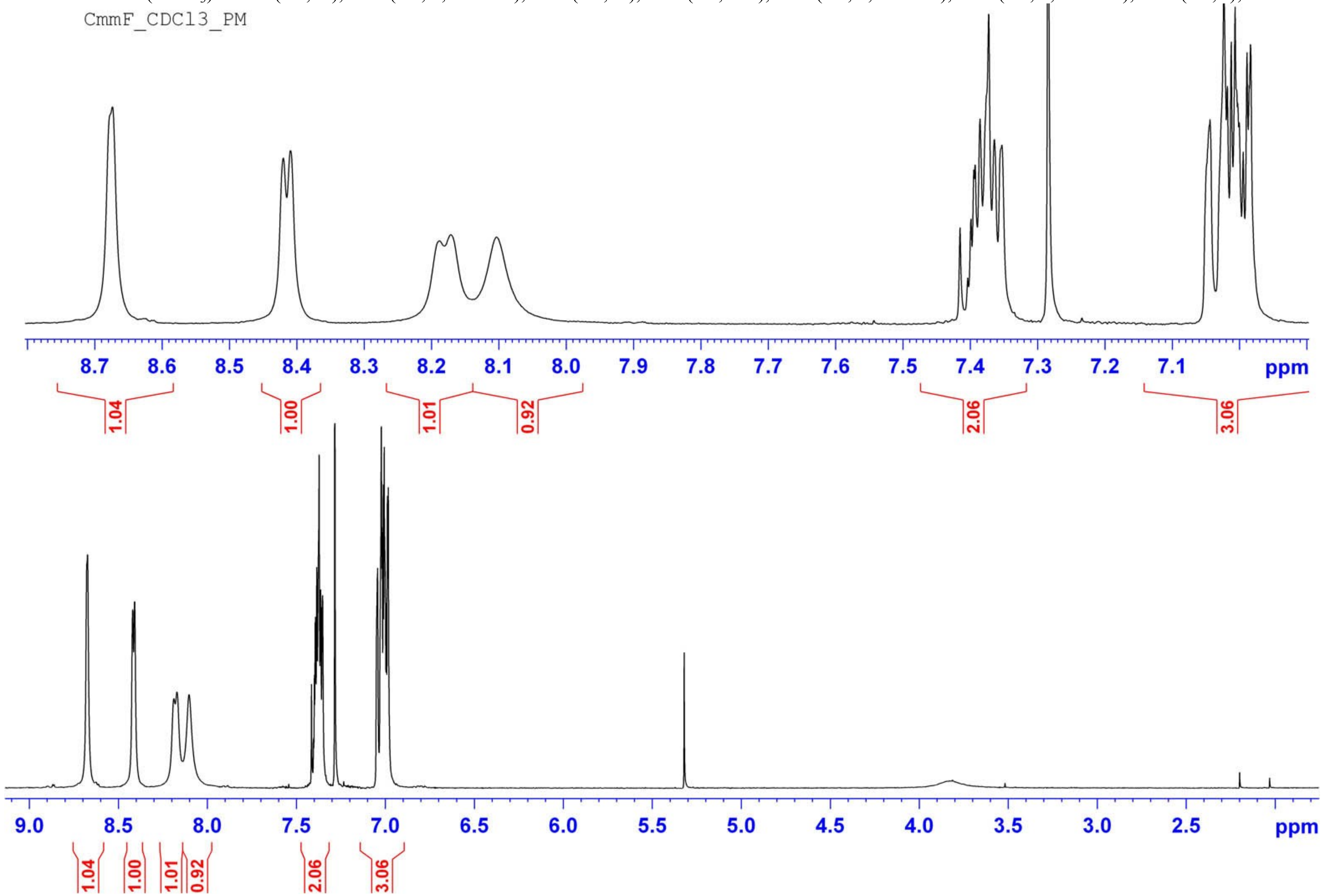




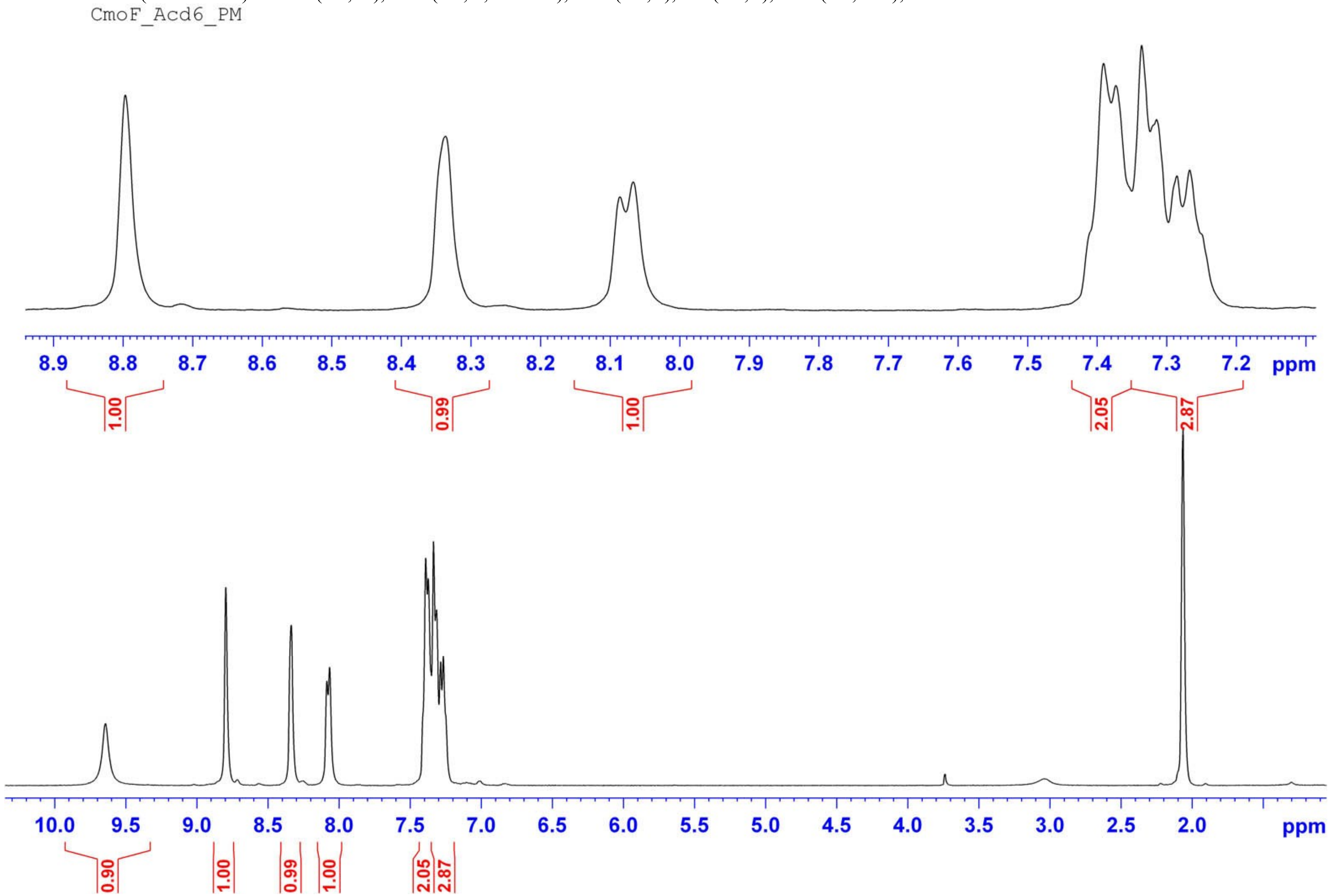
1.1.1.9. **CmmF** (Acetone-d_6): δ 7.08 (1H, tdd, ^3J = 8.5, ^4J = 2.5 ^5J = 0.9), 7.13 (2H, m), 7.38 (1H, dd, ^3J = 8.4, ^4J = 4.8), 7.48 (1H, dd, ^3J = 8.5, ^4J = 6.4), 8.07 (1H, d, ^3J = 8.1), 8.33 (1H, dd, ^3J = 8.4, ^4J = 1.2), 8.79 (1H, d, ^3J = 2.2), 9.52 (1H, br s);



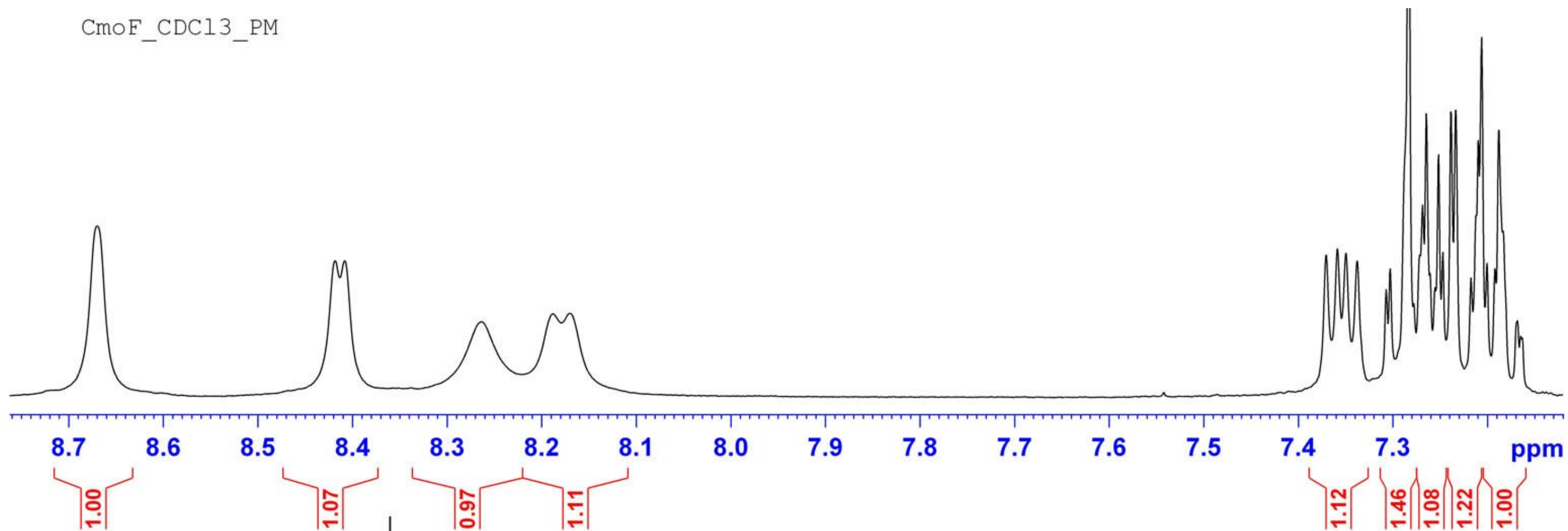
1.1.1.10. **CmmF** ($CDCl_3$) δ 6.99 (2H, m), 7.04 (1H, d, ^3J = 8.1), 7.38 (2H, m), 8.10 (1H, br s), 8.18 (1H, d, ^3J = 7.0), 8.41 (1H, d, ^3J = 4.3), 8.68 (1H, s);

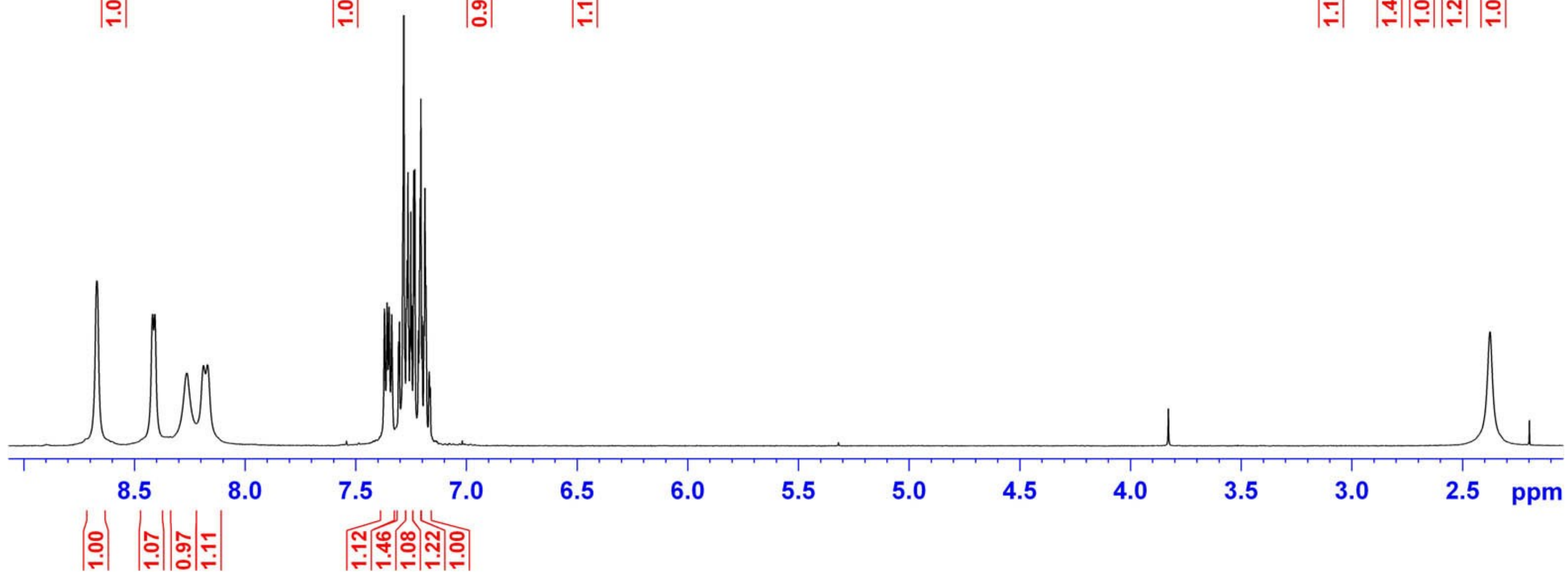


1.1.1.11. **CmoF** (Acetone-d6): δ 7.32 (5H, m), 8.08 (1H, d, ^{4}J = 7.8), 8.34 (1H, s), 8.8 (1H, s), 9.64 (1H, br s);

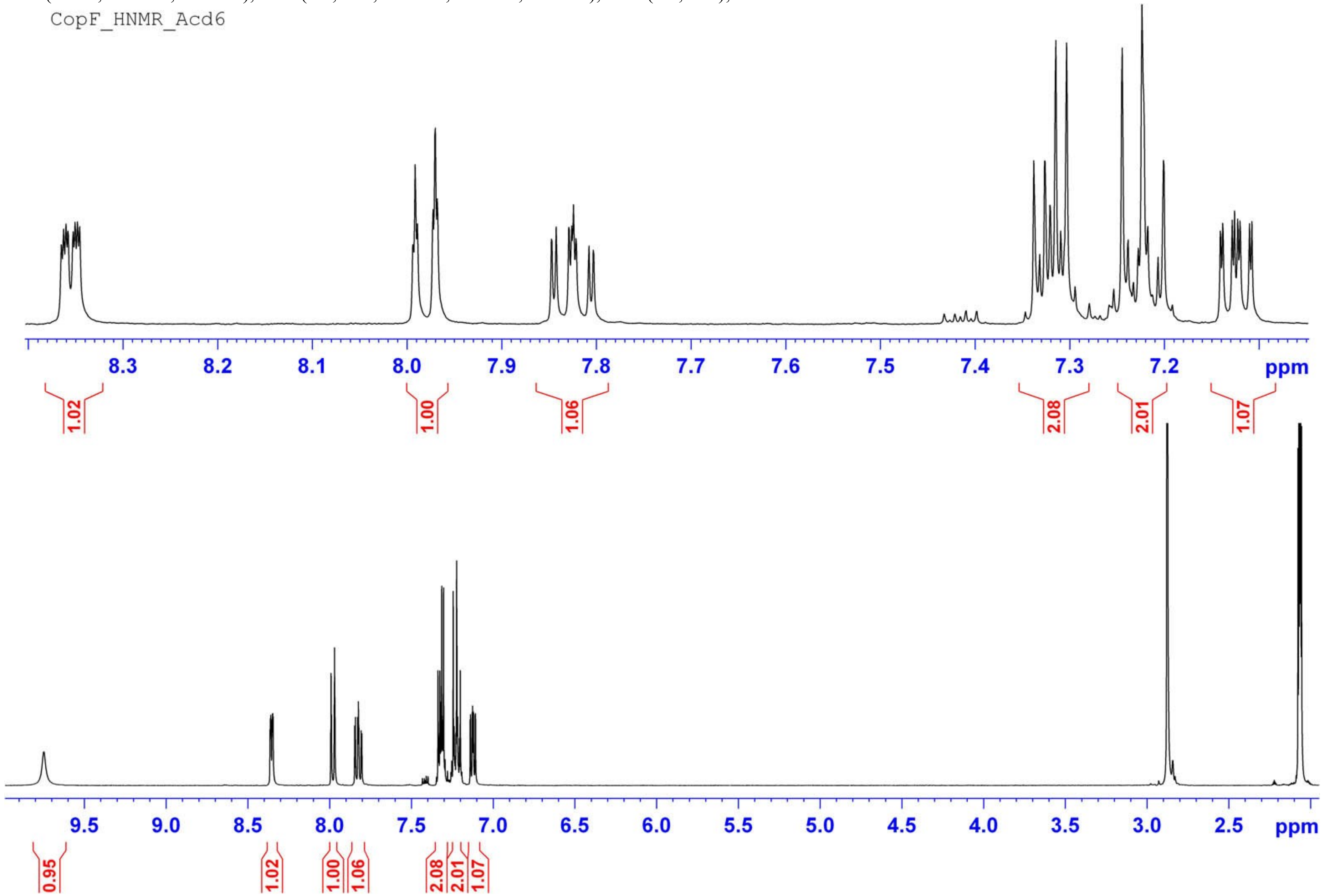


1.1.1.12. **CmoF** ($CDCl_3$) δ 7.22 (4H, m; including residual $CHCl_3$ solvent), 7.35 (1H, dd, $^3J = 8.5$, $^4J = 4.7$), 8.18 (1h, d, ^3J =7.2), 8.26 (1H, br s), 8.41 (1H, d, ^3J = 4.2), 8.67 (1H, br s);

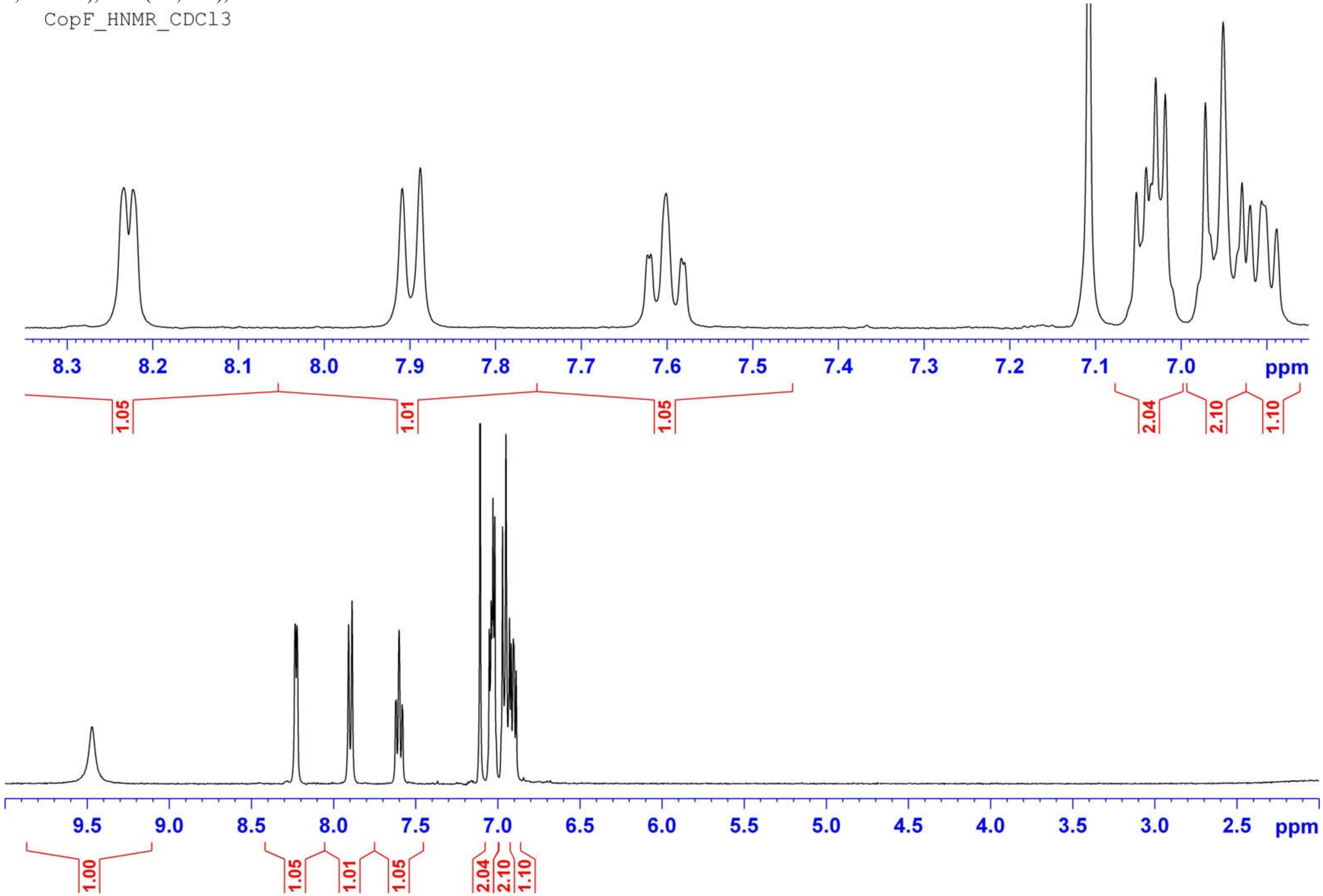




1.1.1.13. **CopF** (Acetone-d6): δ 7.12 (1H, ddd, $^{3}J = 7.7$, $^{4}J = 4.9$, $^{5}J = 1.0$), 7.22 (2H, tt, $^{3}J = 8.8$, $^{4}J = 2.4$), 7.32 (2H, m), 7.82 (1H, ddd, $^{3}J = 8.4$, $^{4}J = 7.3$, $^{5}J = 2$), 7.98 (1H dt, $^{3}J = 8.5$, $^{4}J = 0.9$), 8.35 (1H, ddd, $^{3}J = 4.9$, $^{4}J = 1.9$, $^{5}J = 0.8$), 9.75 (1H, br s);

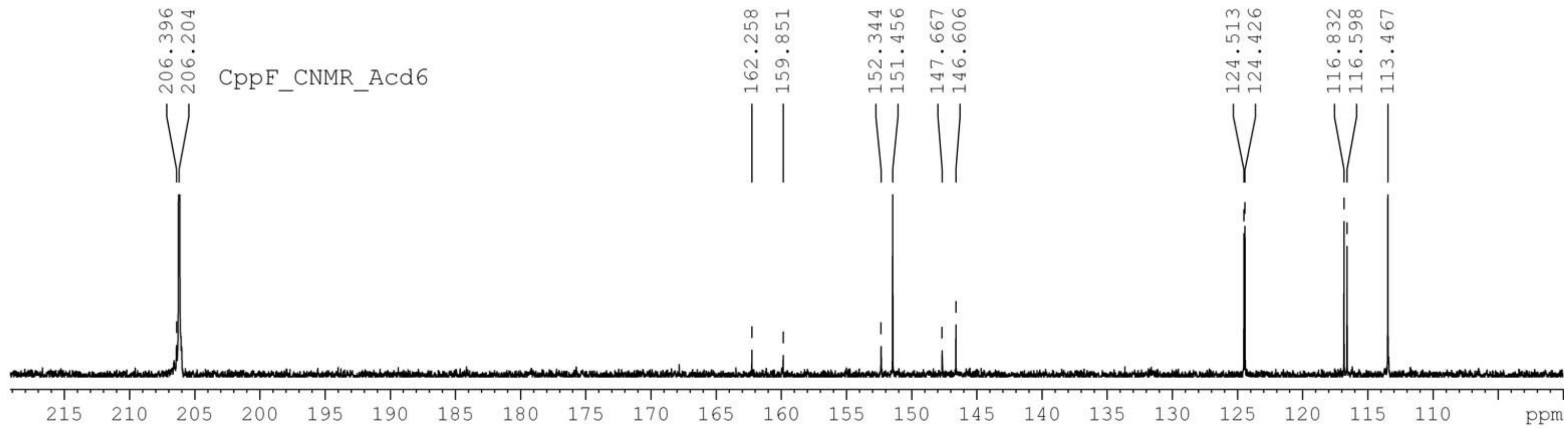


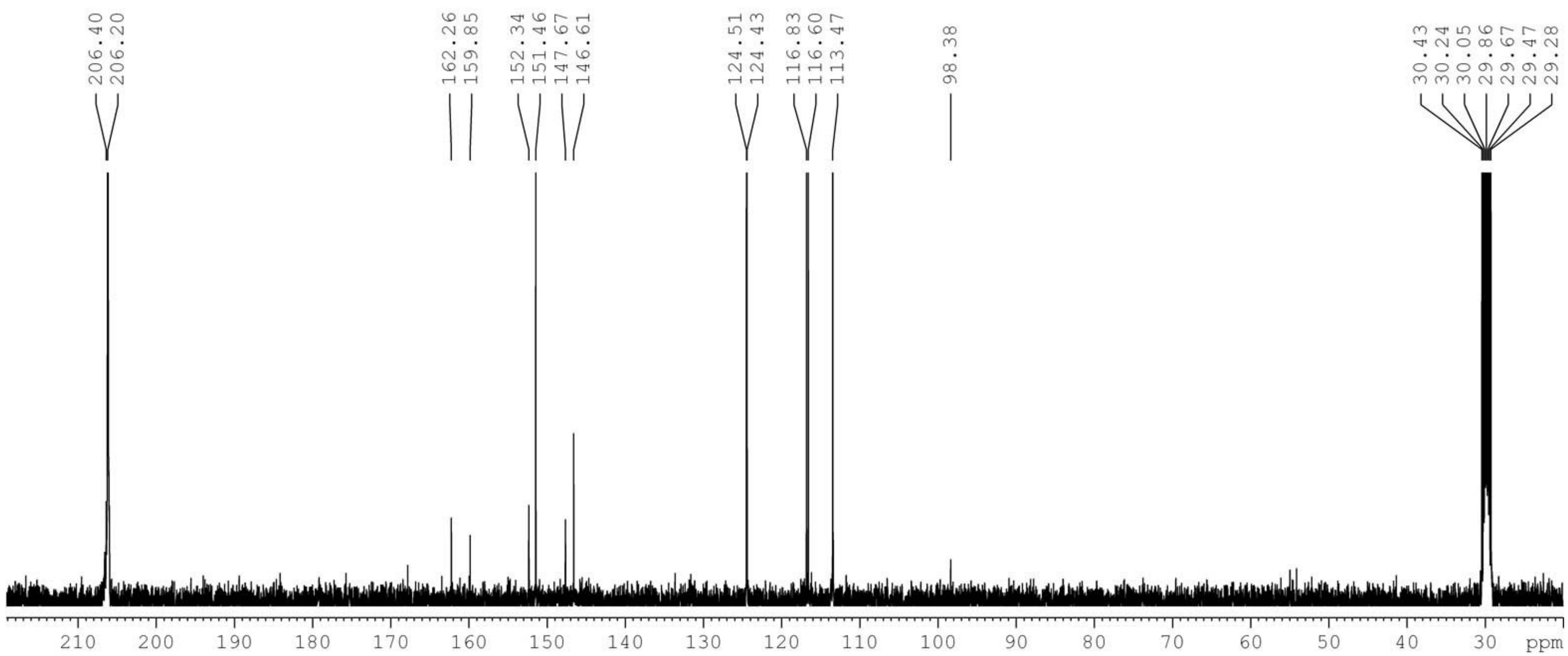
1.1.1.14. **CopF** ($CDCl_3$) δ 6.90 (1H, dd, ^3J = 7.5, ^4J = 5.4), 6.95, (2H, t, ^3J = 8.5), 7.03 (2H, m), 7.60 (1H, td, ^3J = 7.8, ^4J = 1.5), 7.90 (1H, d, ^3J = 8.5), 8.23 (1H, d, ^3J = 4.3), 9.47 (1H, br s);



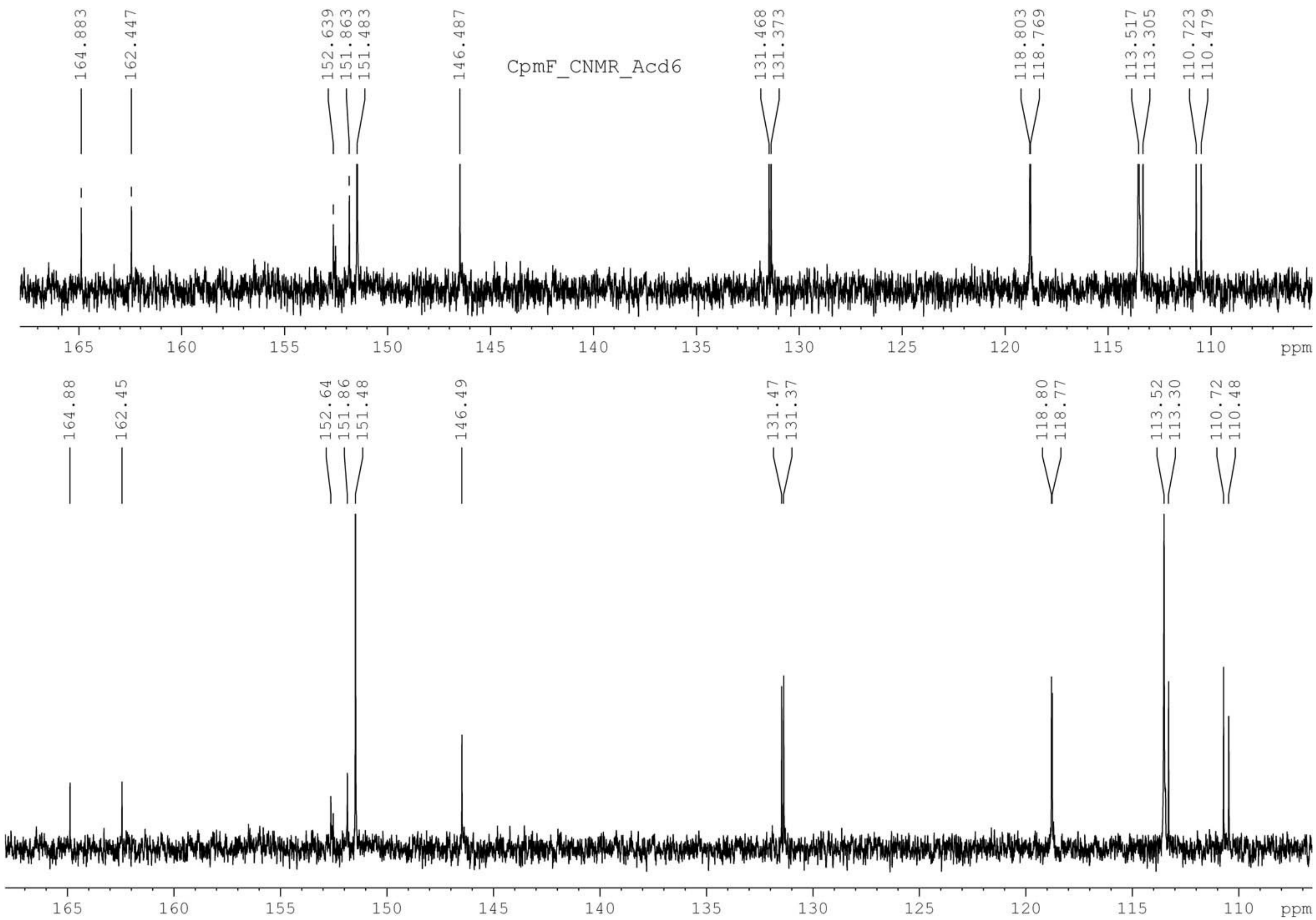
1.1.2. ^{13}C NMR data and spectra (400 MHz, Acetone-d_6)

1.1.2.1. **CppF**: δ 113.46, 116.60/116.83, 124.43/124.51, 146.61, 147.67, 151.46, 152.34, 159.85, 162.26;

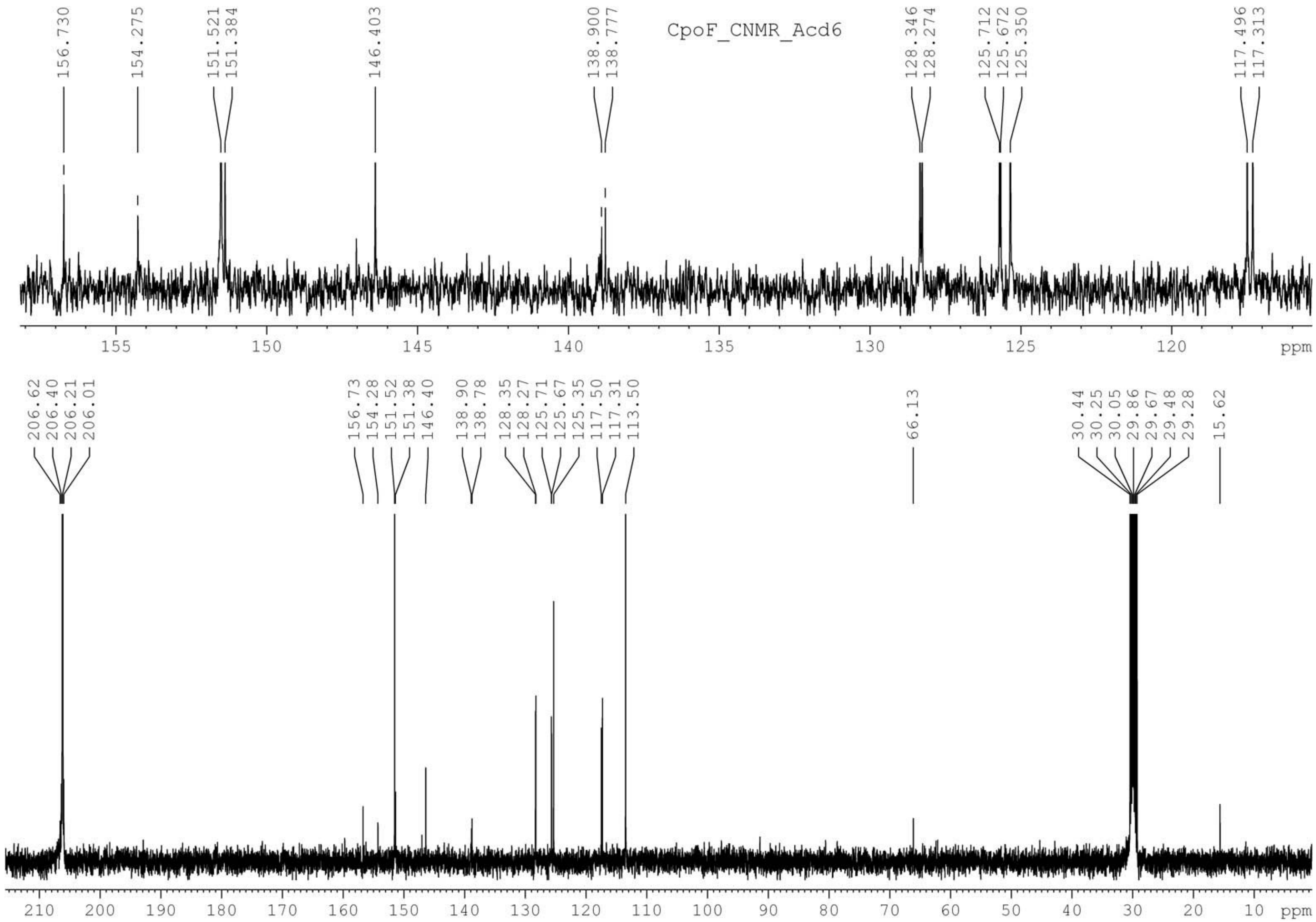




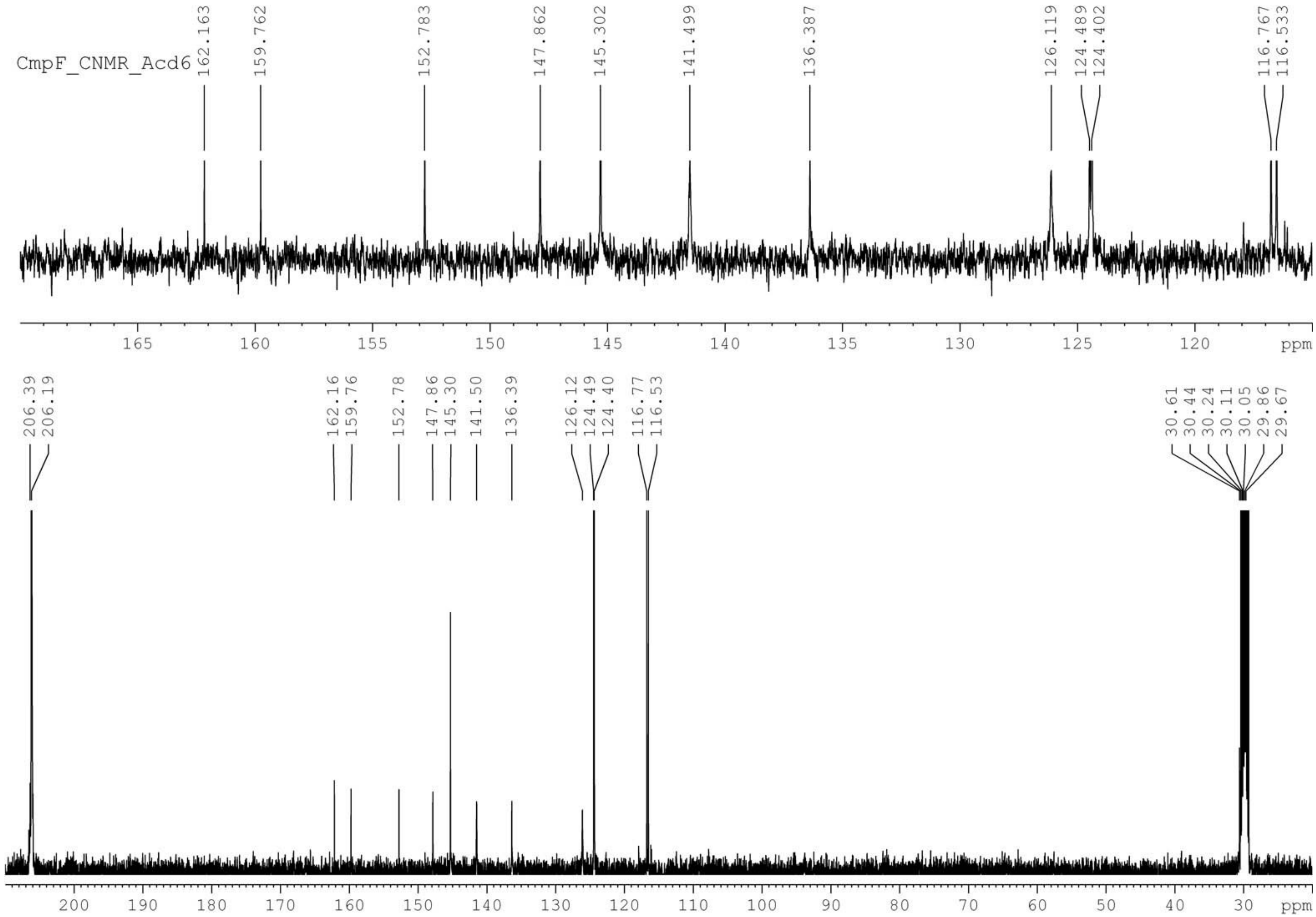
1.1.2.2. **CpmF**: δ 110.48/110.72, 113.30/113.51, 118.77/118.80, 131.37/131.47, 146.49, 151.48, 151.86, 152.64, 162.45, 164.88;



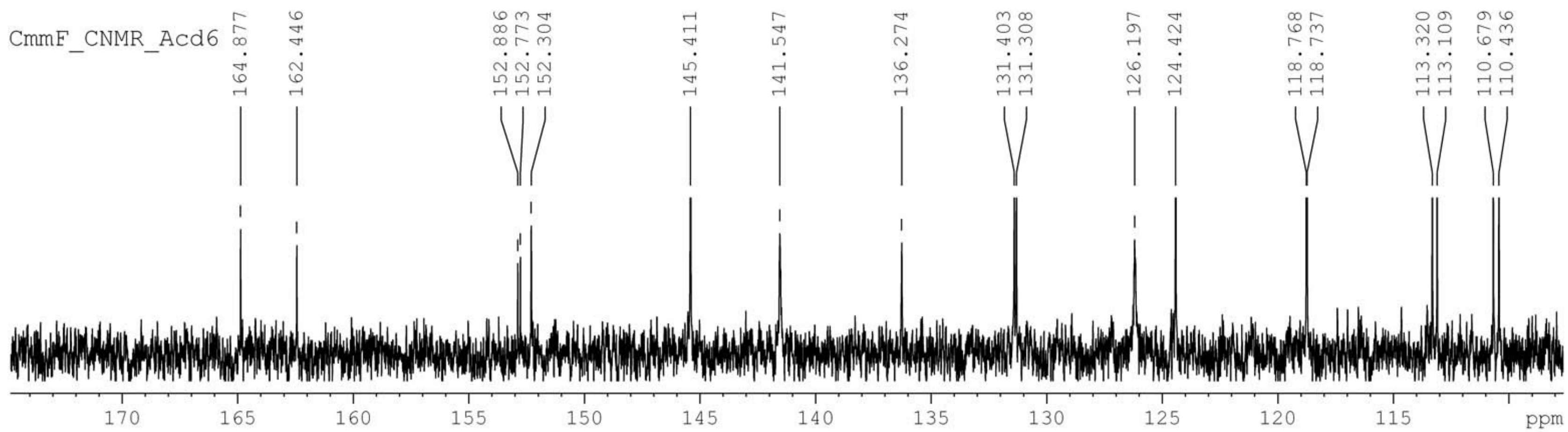
1.1.2.3. **CpoF**: δ 117.31, 117.50, 125.35, 125.67/125.71, 128.27/128.35, 138.78/138.90, 146.40, 151.38/151.52, 154.75, 156.73;

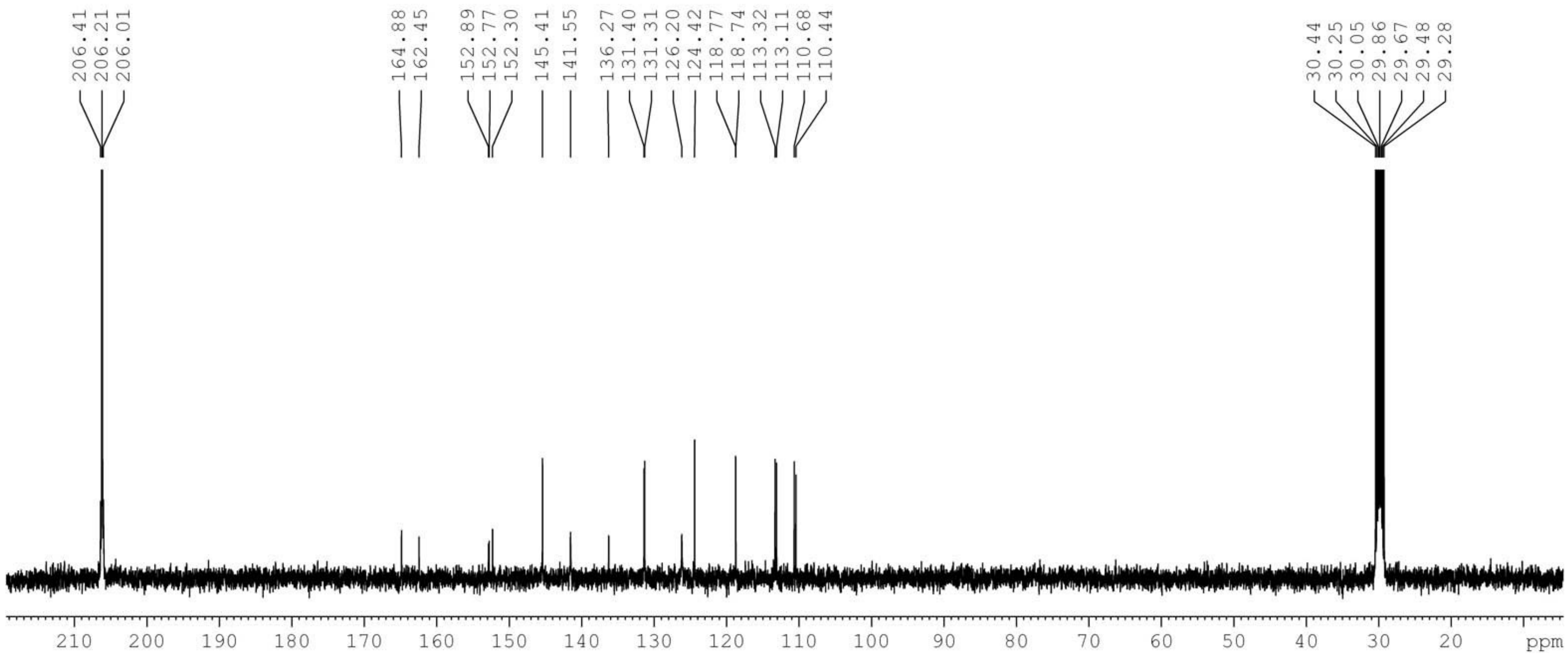


1.1.2.4. **CmpF**: δ 116.53/116.77, 124.40/124.50, 126.12, 136.39, 141.50, 145.30, 147.86, 152.78, 159.76, 162.16;

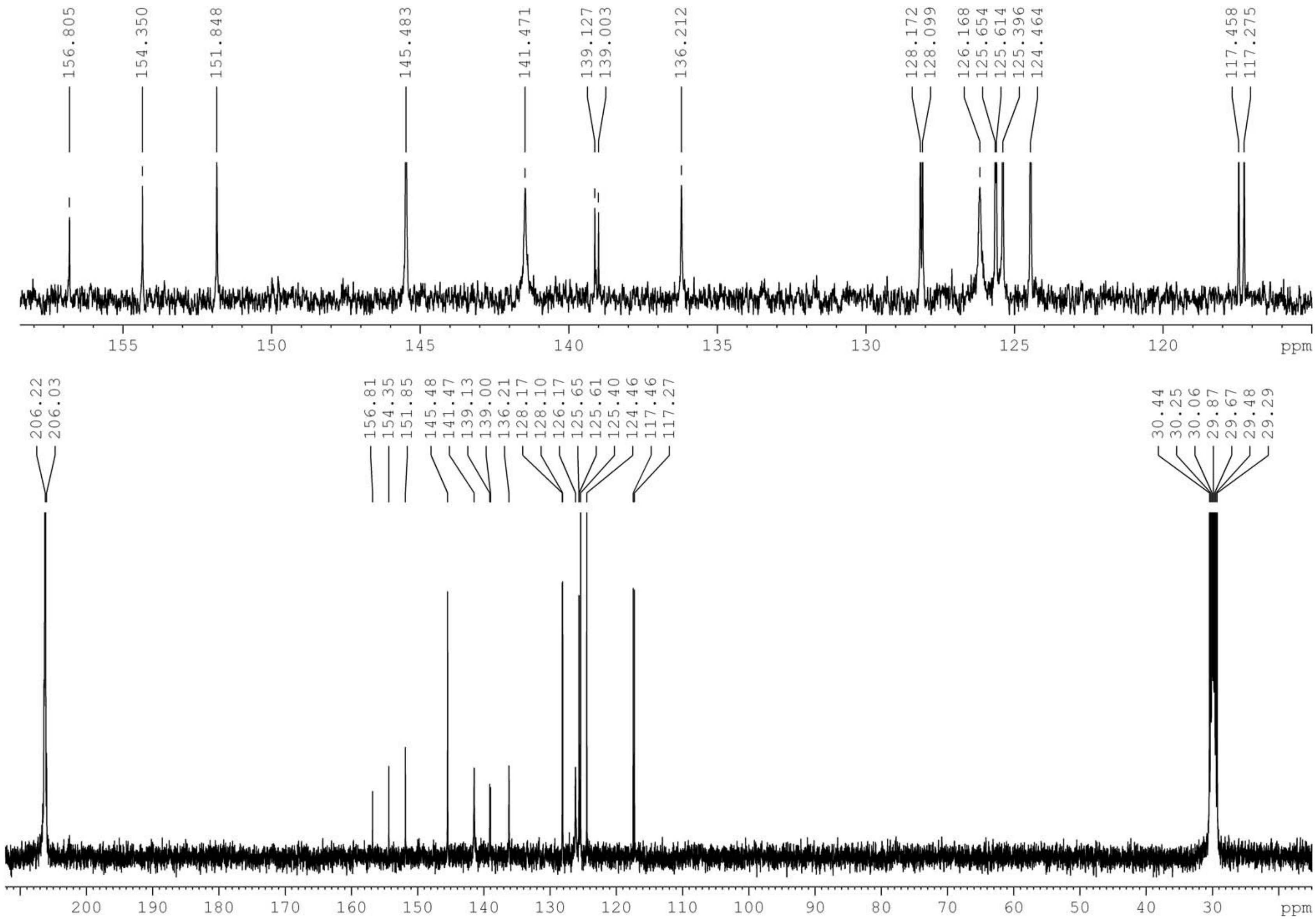


1.1.2.5. **CmmF**: δ 110.44/110.68, 113.11/113.32, 118.74/118.77, 124.42, 126.20, 131.31/131.40, 136.27, 141.55, 145.41, 152.30, 152.77/152.89, 162.45/164.88;

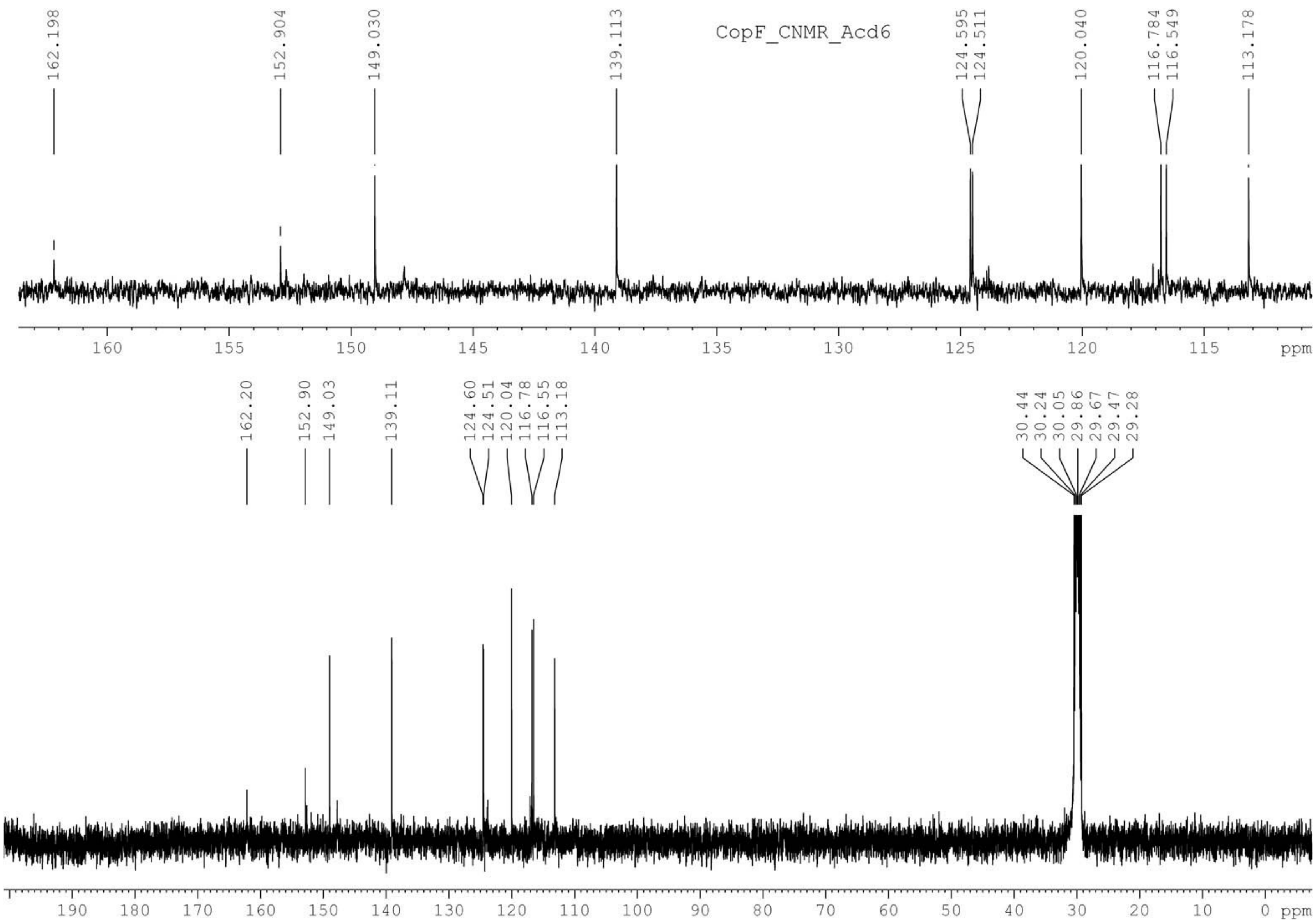




1.1.2.6. **CmoF**: δ 117.27/117.46, 124.46, 125.40/125.61/125.65, 126.17, 128.10/128.17, 136.21, 139.00/139.12, 141.47, 145.48, 151.85, 154.35, 156.80;

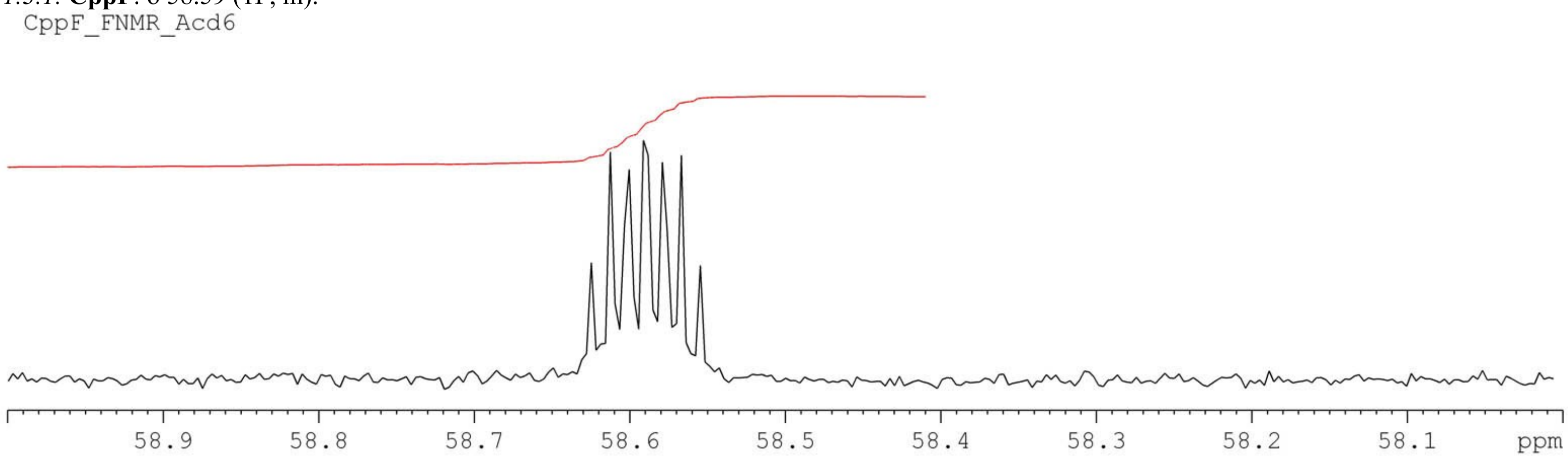


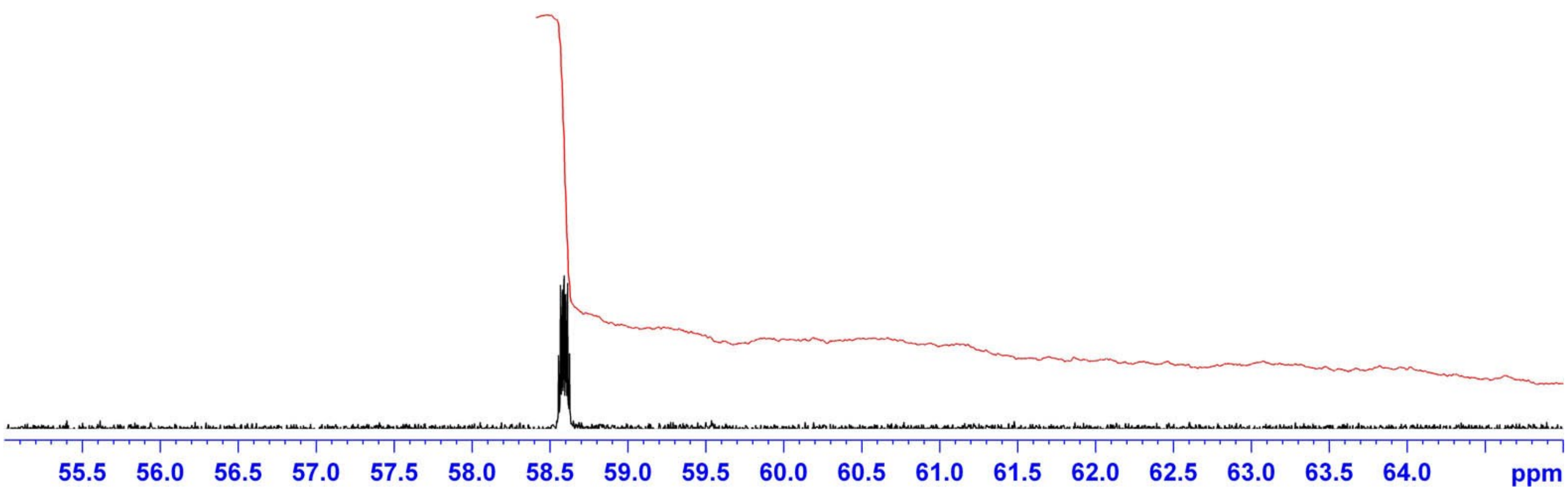
1.1.2.7. **CopF**: δ 113.18, 116.55, 116.78, 120.04, 124.51, 124.59, 139.11, 149.03, 152.90, 162.20;



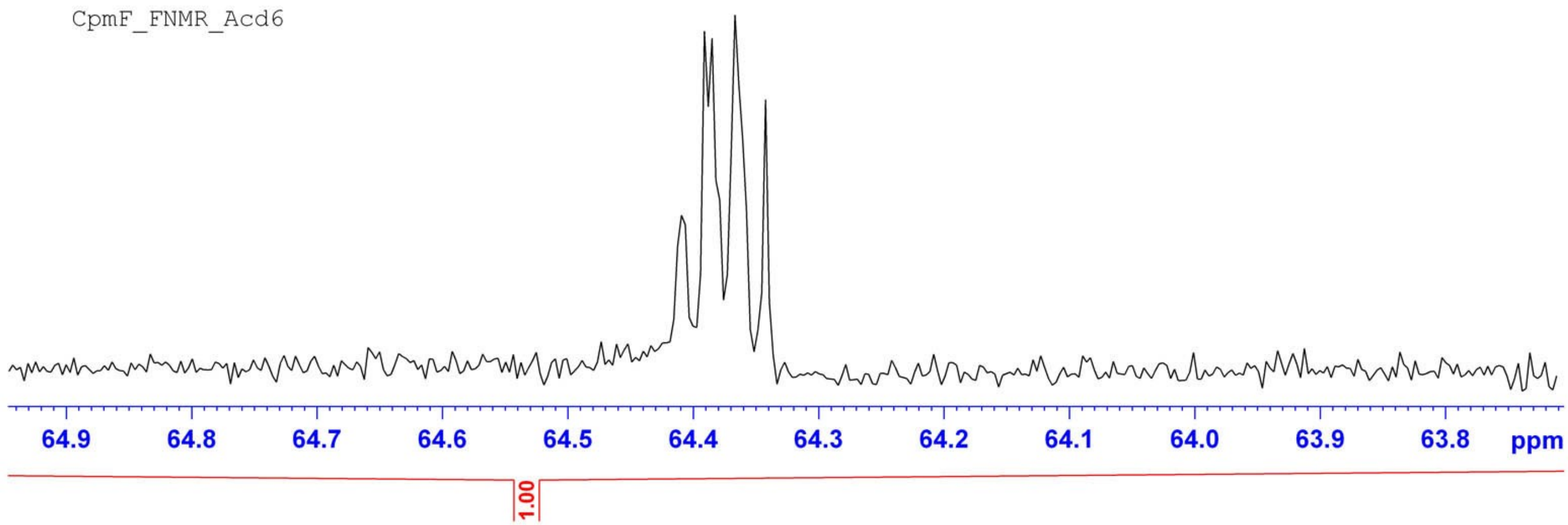
1.1.3. ^{19}F NMR data and spectra (400 MHz, Acetone-d_6)

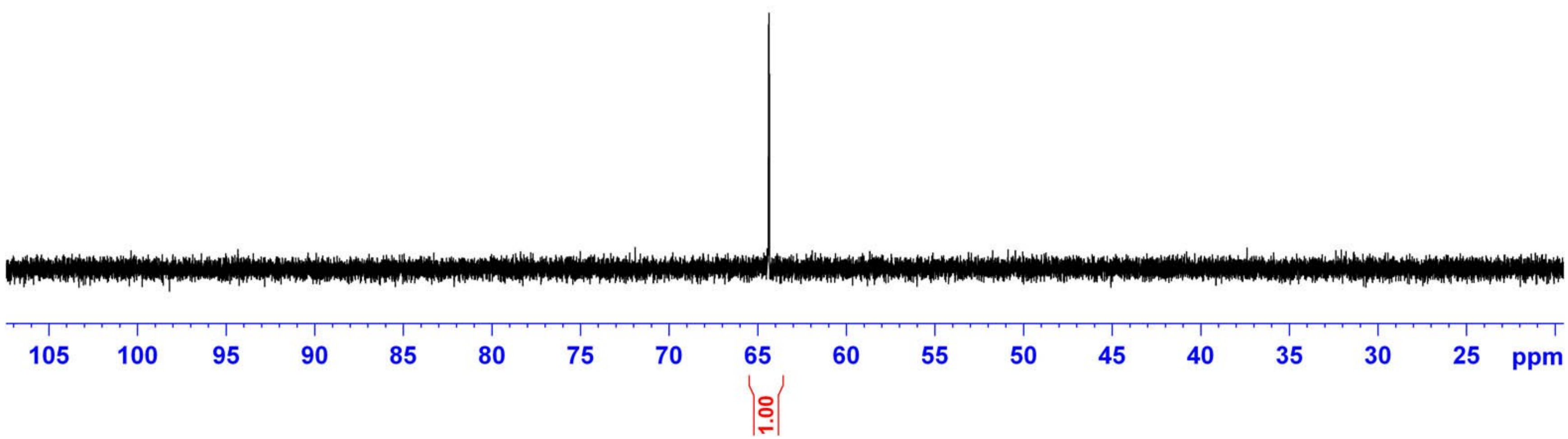
1.1.3.1. **CppF**: δ 58.59 (1F, m).



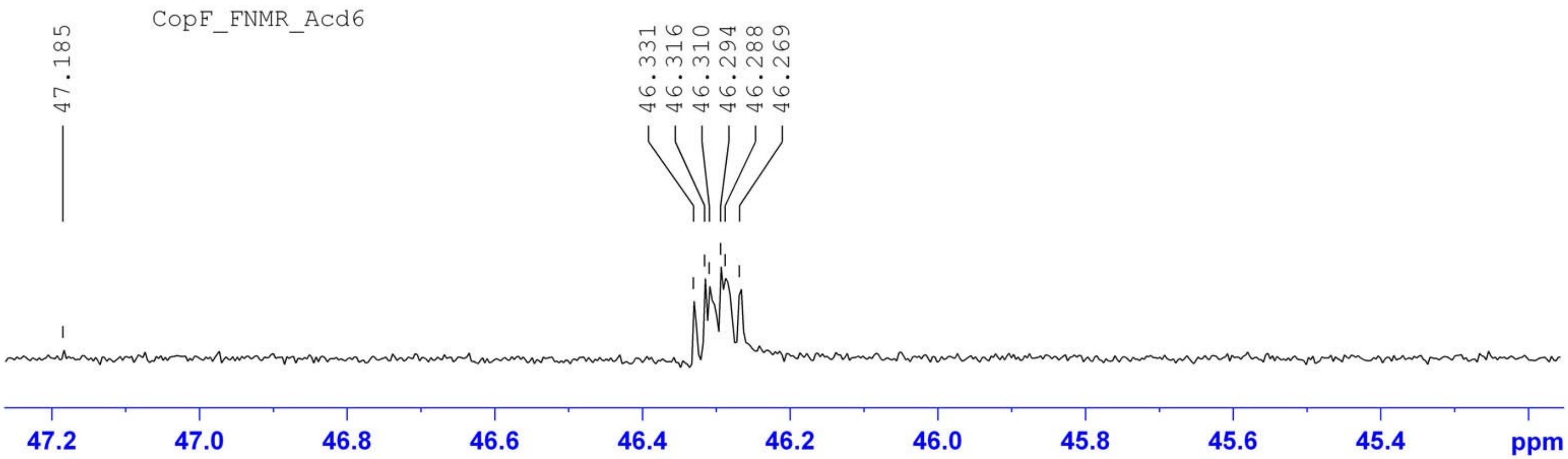


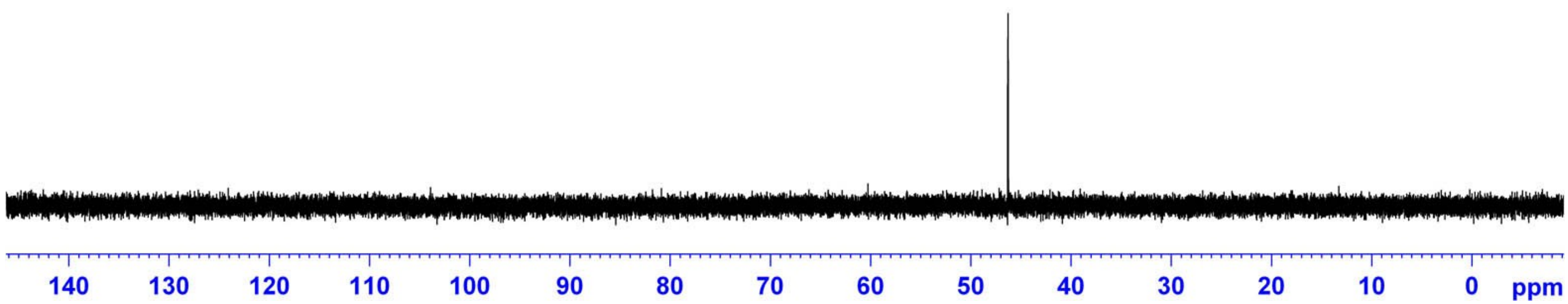
1.1.3.2. **CpmF**: δ 64.38 (1F, m)



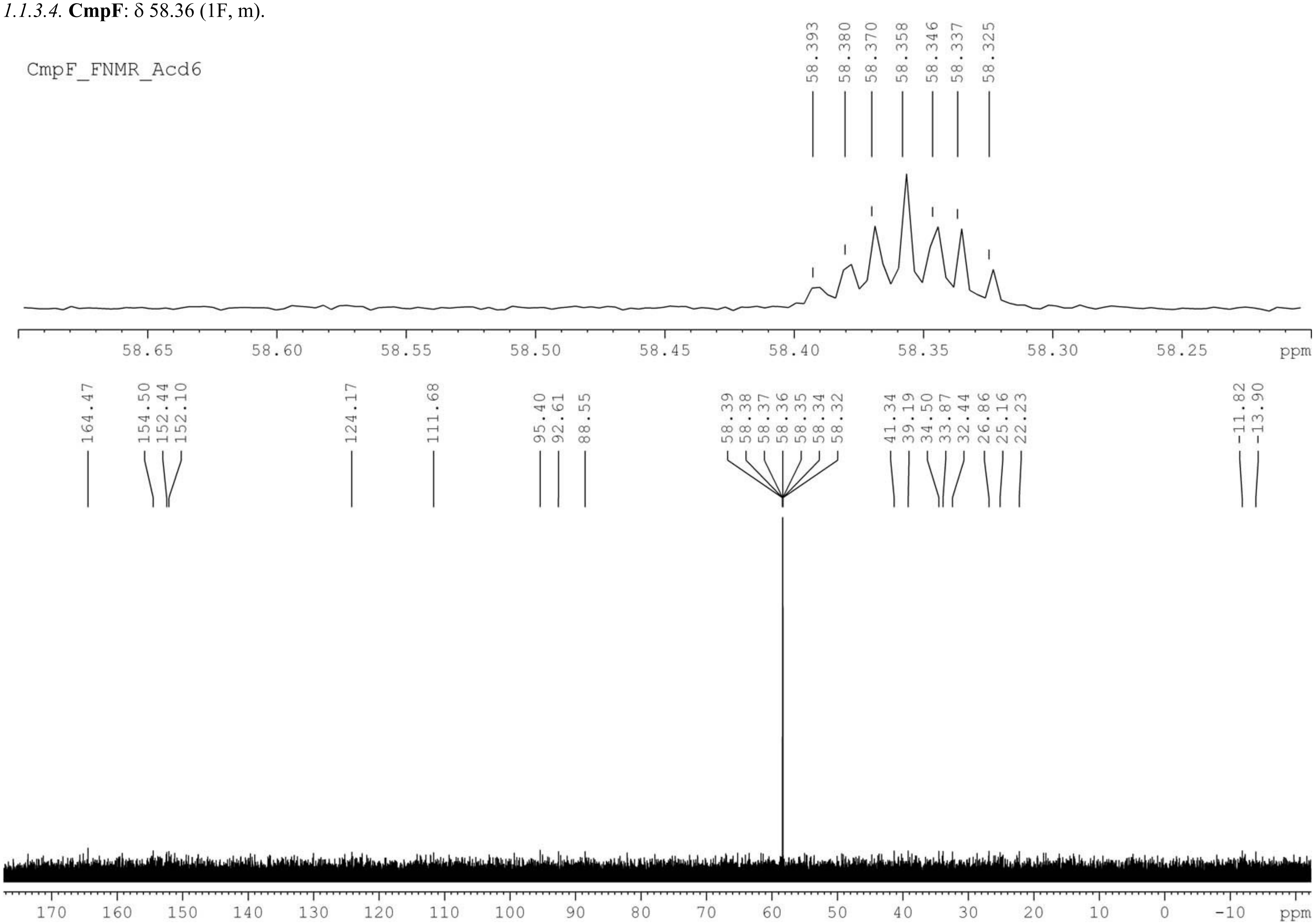


1.1.3.3. **CpoF**: δ 46.29 (1F, m)

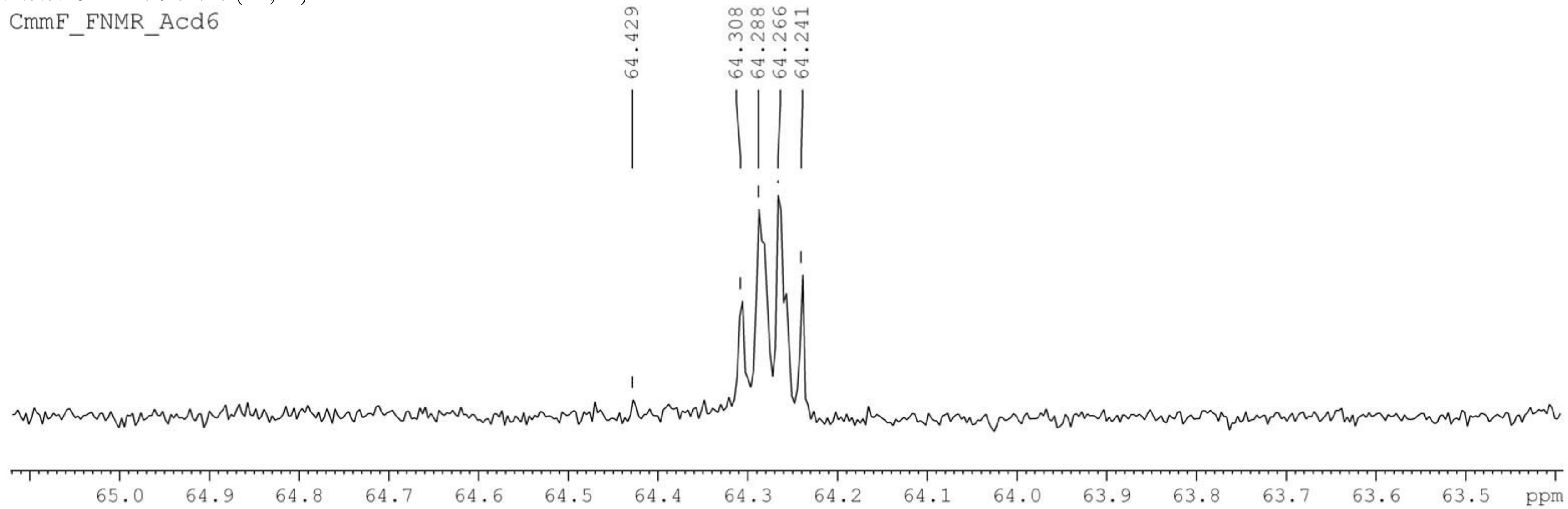


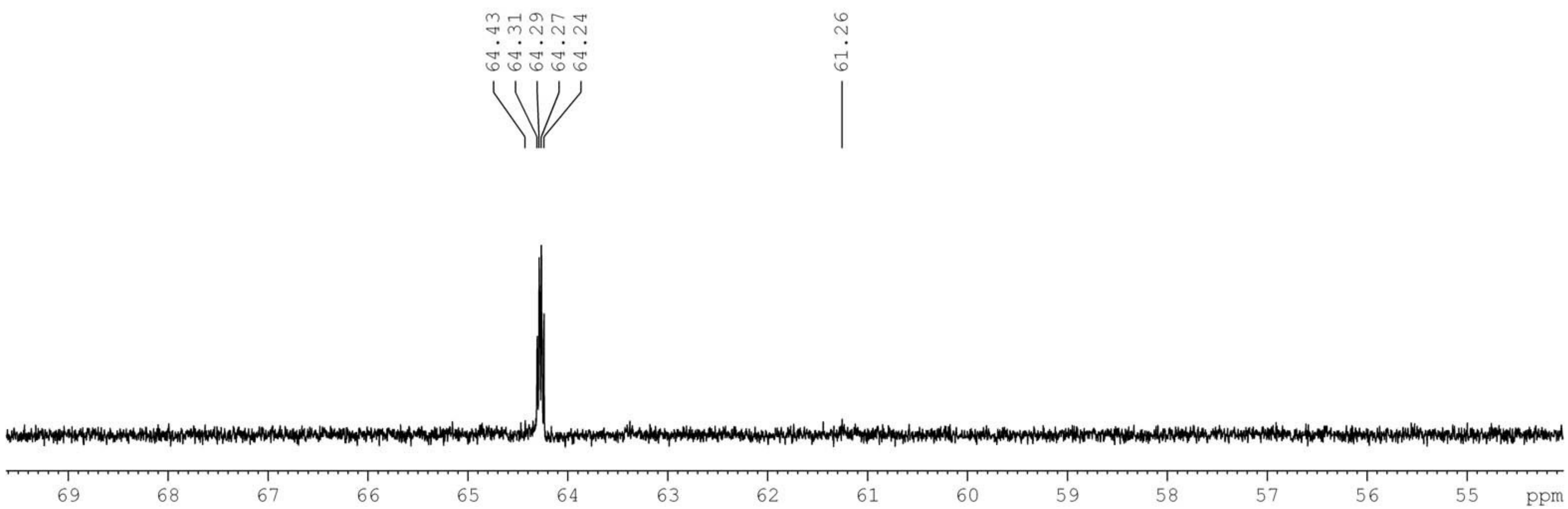


1.1.3.4. **CmpF**: δ 58.36 (1F, m).

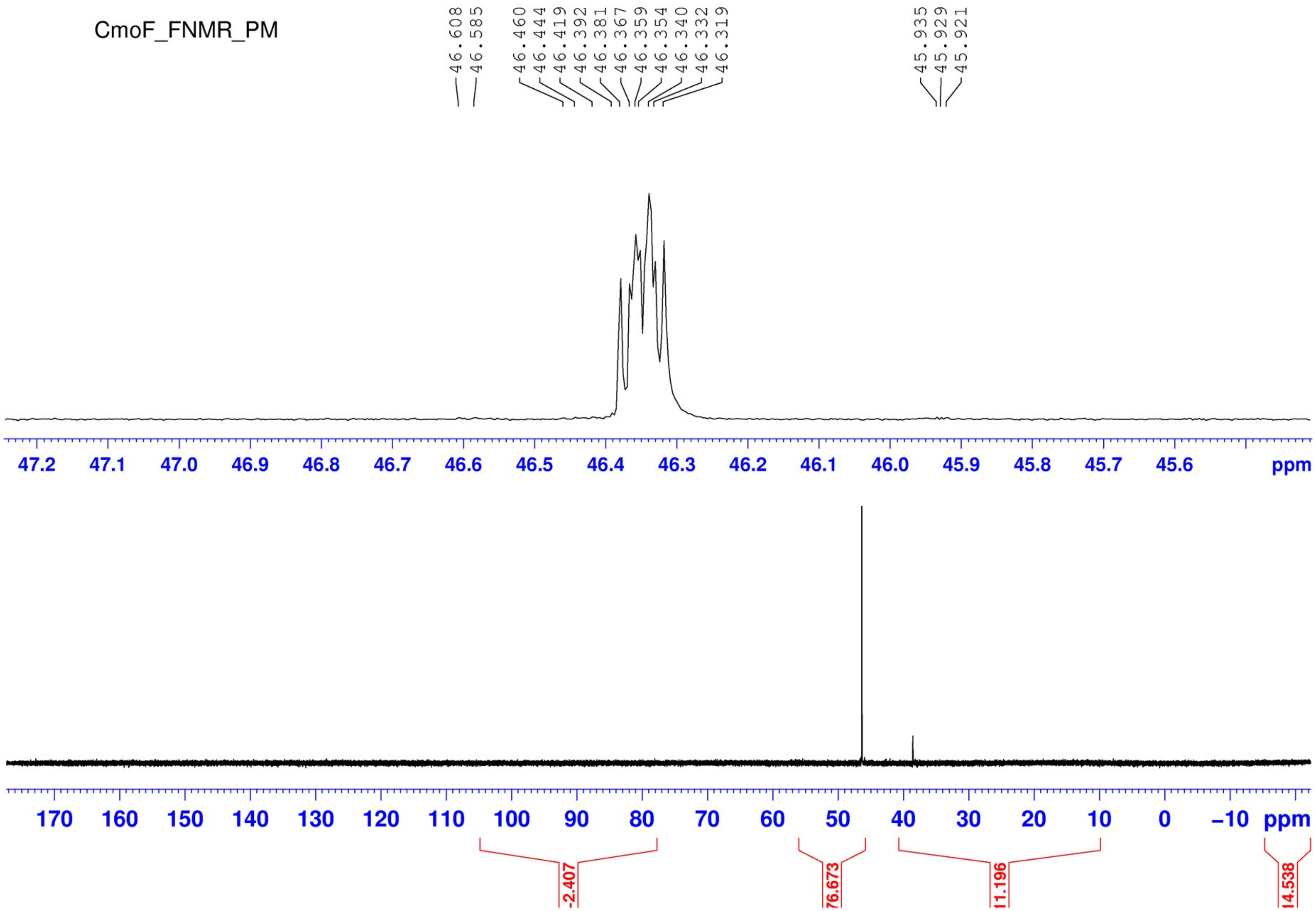


1.1.3.5. **CmmF**: δ 64.28 (1F, m)

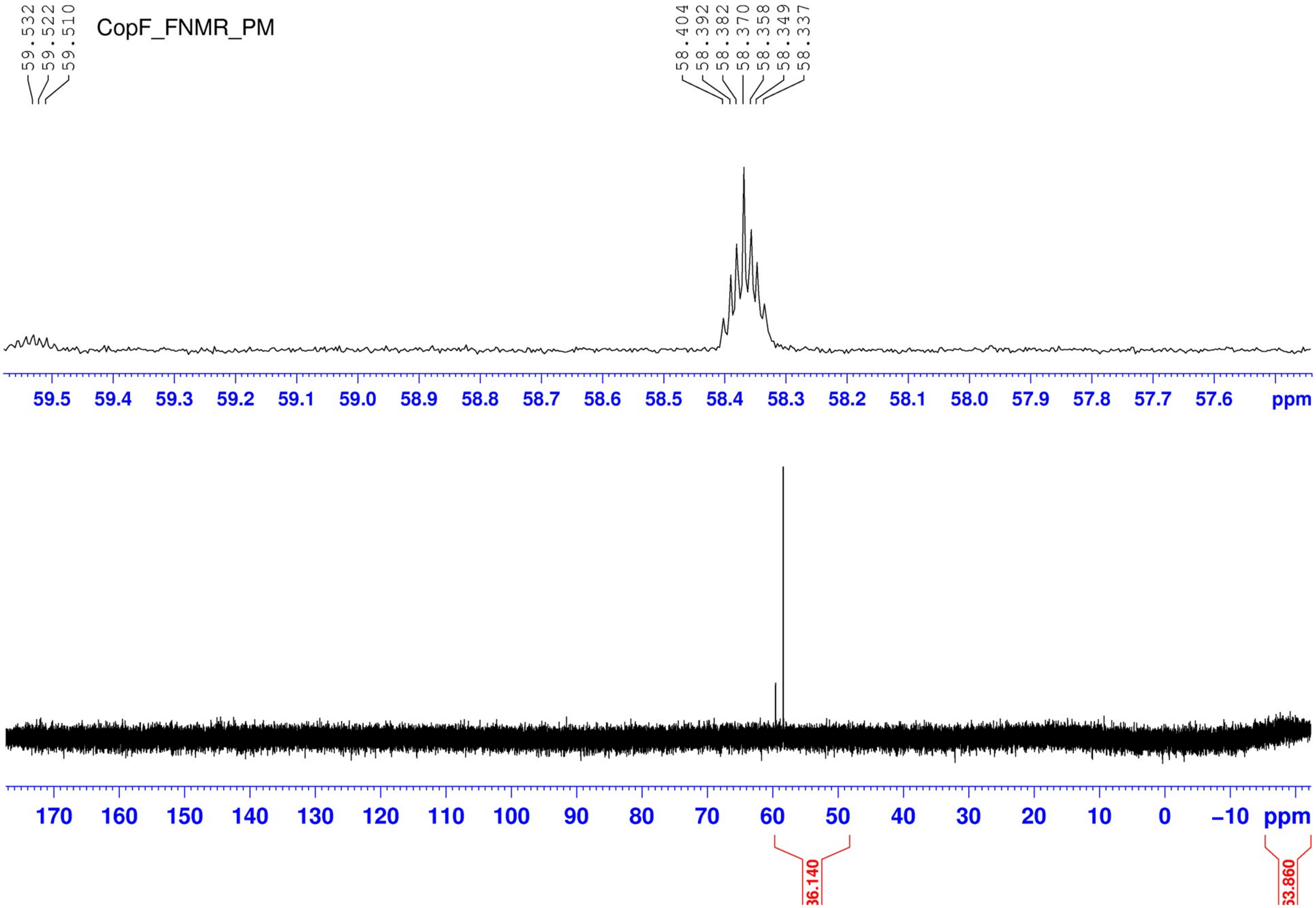




1.1.3.6. **CmoF**: δ 46.36 (1H, m);

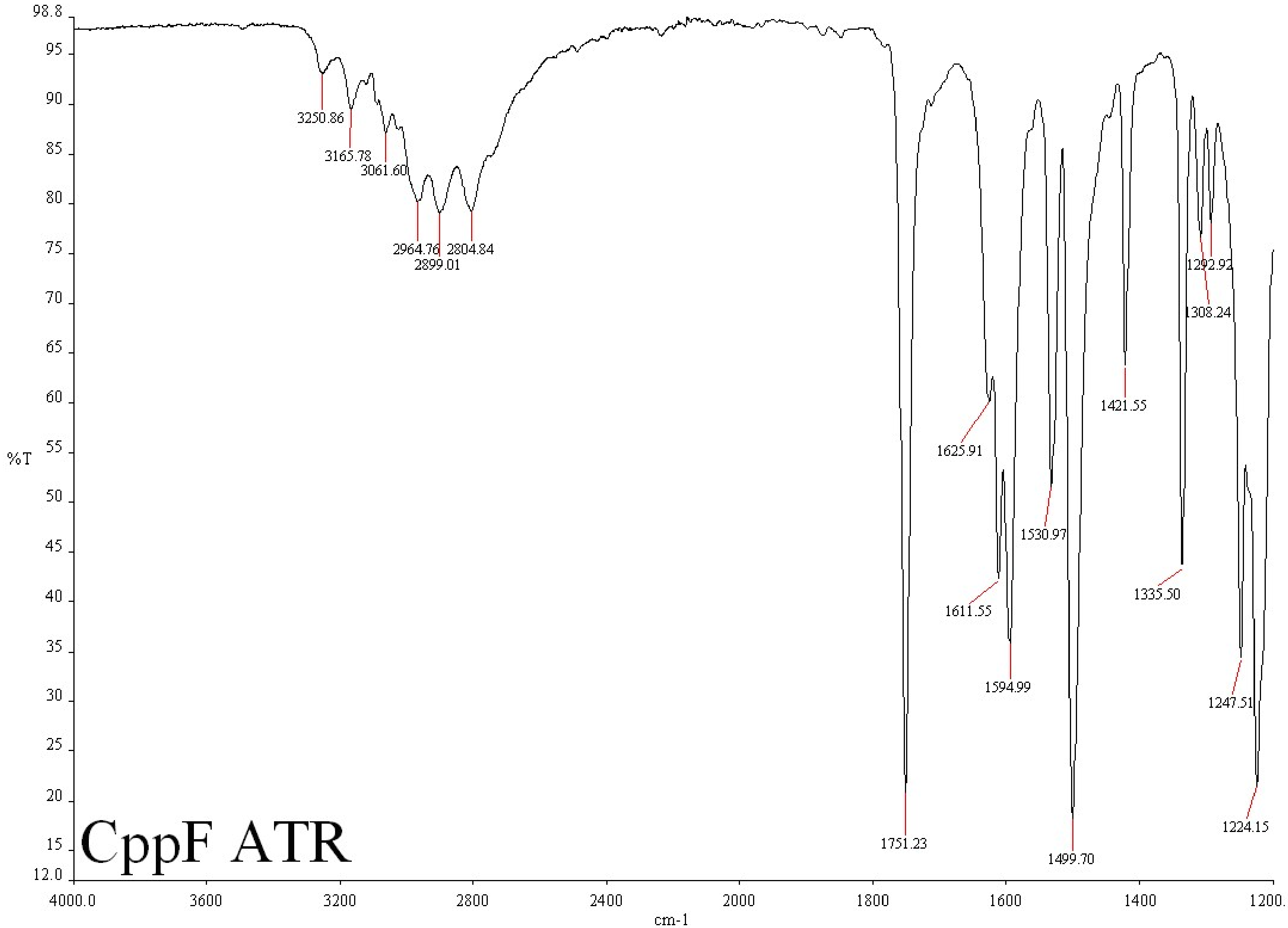


1.1.3.7. **CopF**: δ 58.37 (1H, m);

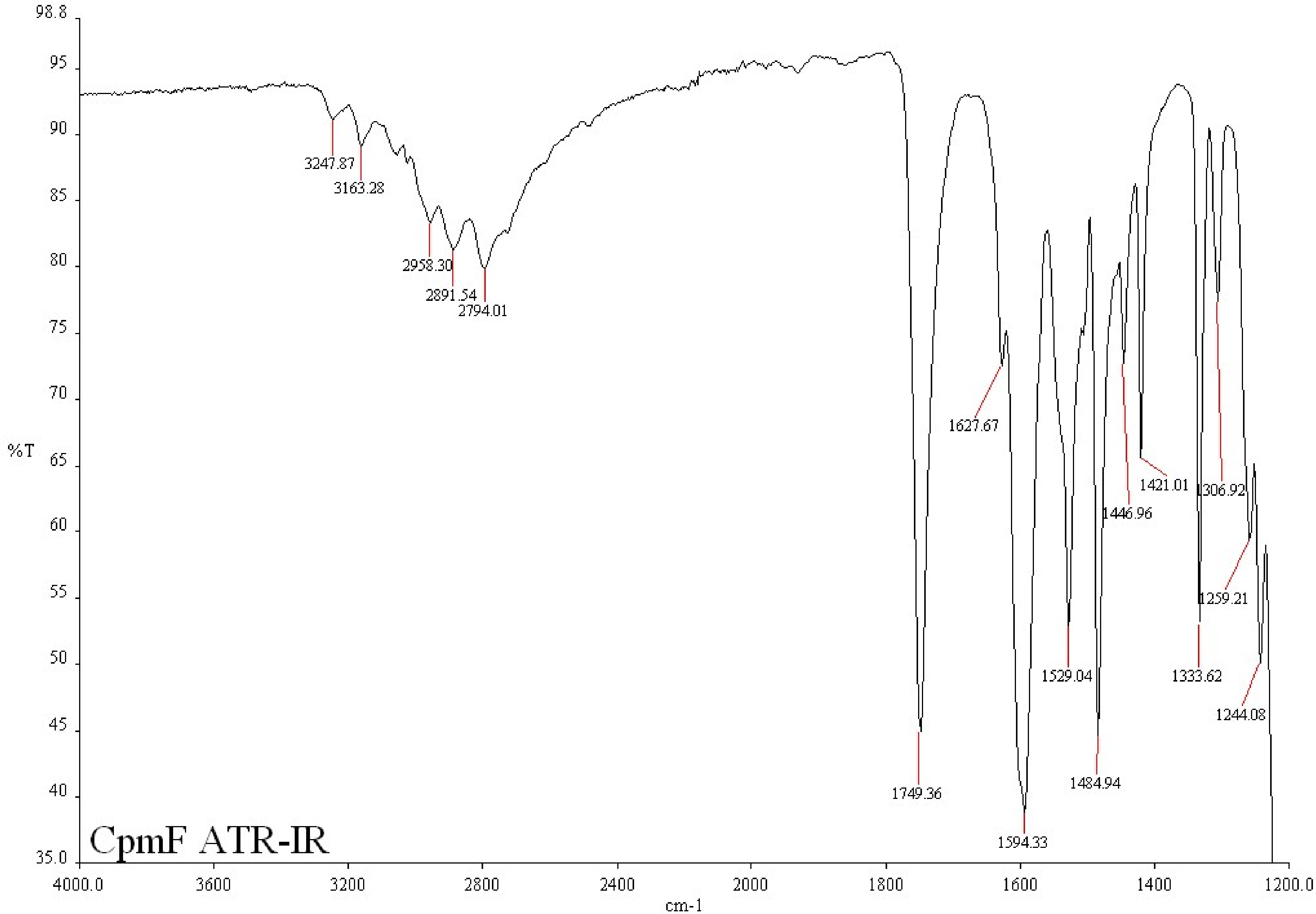


1.1.4. <u>IR (ATR) data and spectra</u>

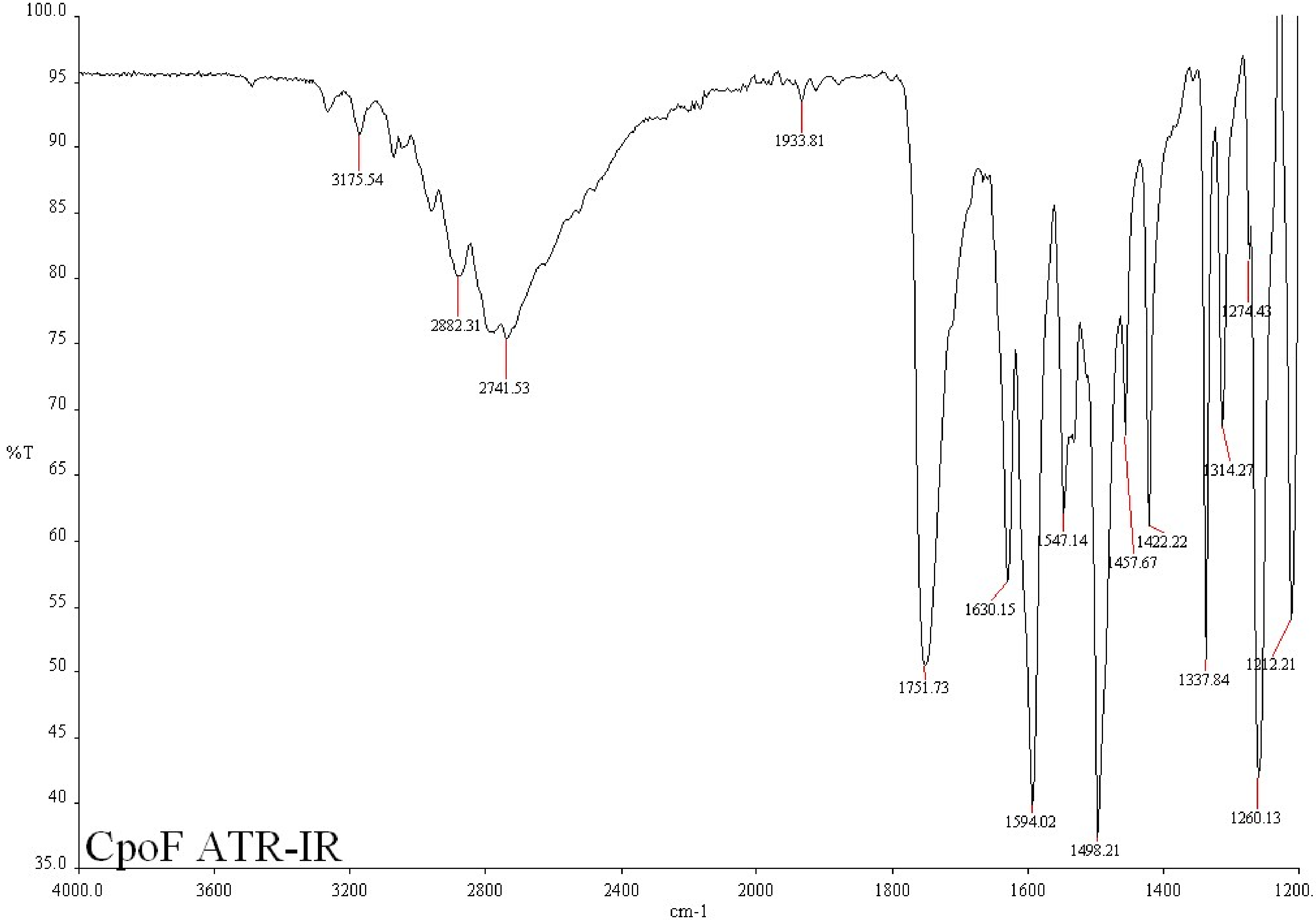
1.1.4.1. **CppF**: 3251 (w), 3166 (w), 3032 (w), 2965 (w), 2899 (w), 2805 (w), 1751 (s), 1626 (m), 1611 (s), 1595 (s), 1531 (m), 1499 (s), 1421 (m).



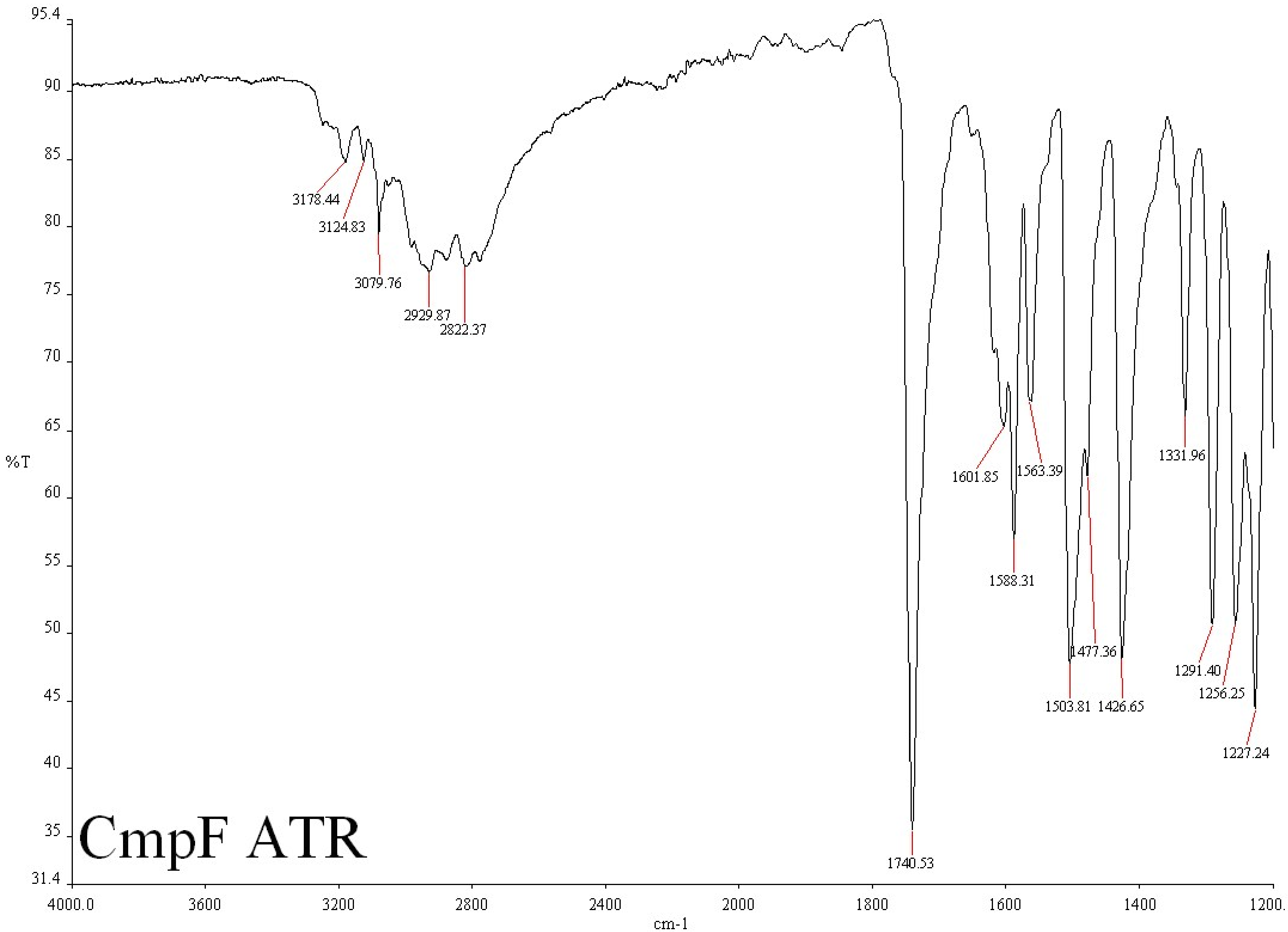
1.1.4.2. **CpmF**: 3248 (w), 3163 (w), 2958 (m), 2891 (m), 2794(m), 1749 (s), 1628 (m), 1594 (s), 1529 (s), 1485 (s), 1447 (m), 1421 (m).



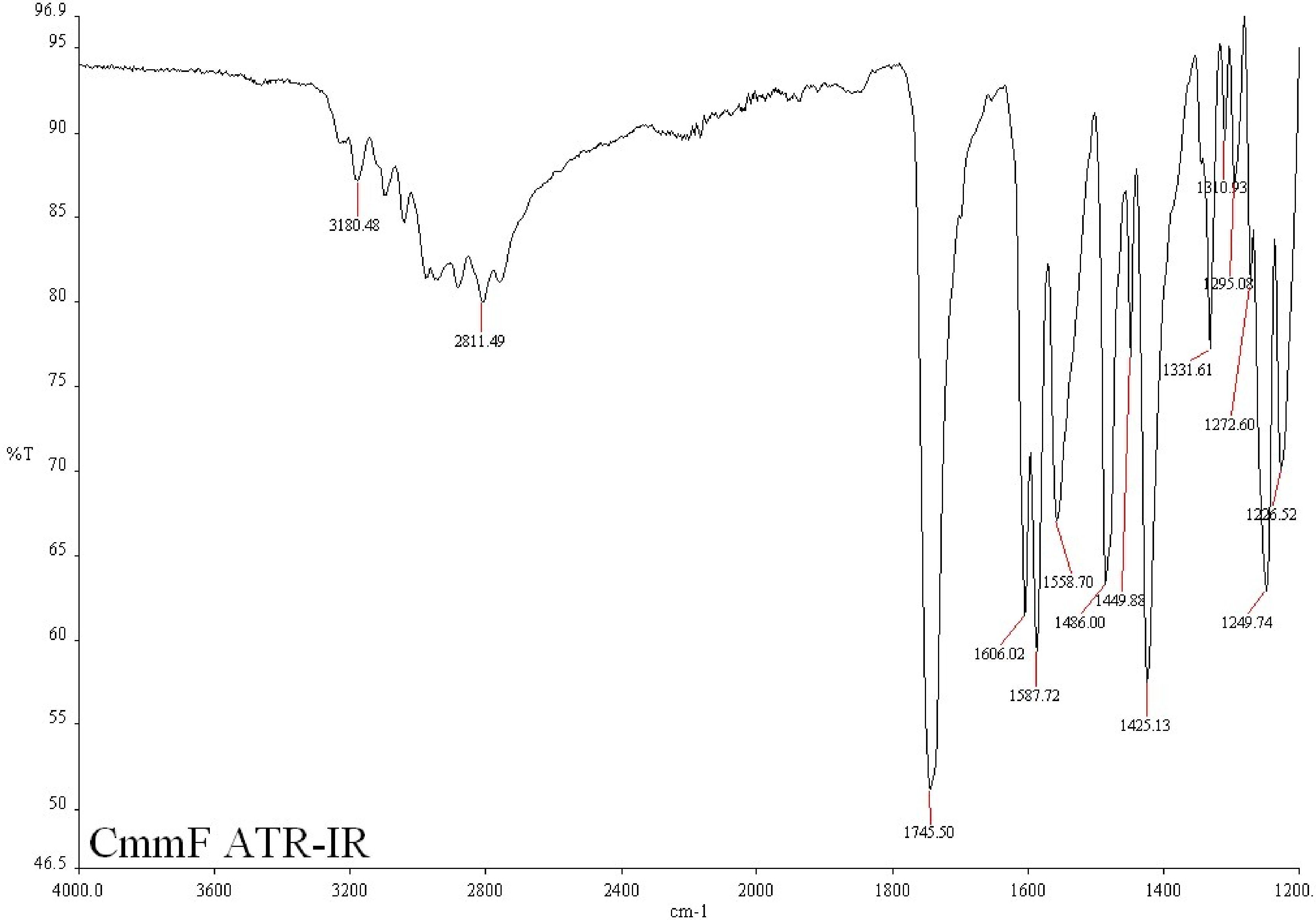
1.1.4.3. **CpoF**: 3176 (w), 2882 (m), 2741 (m), 1934 (w), 1752 (s), 1630 (s), 1594 (s), 1547 (m), 1498 (s), 1458 (m), 1422 (m).



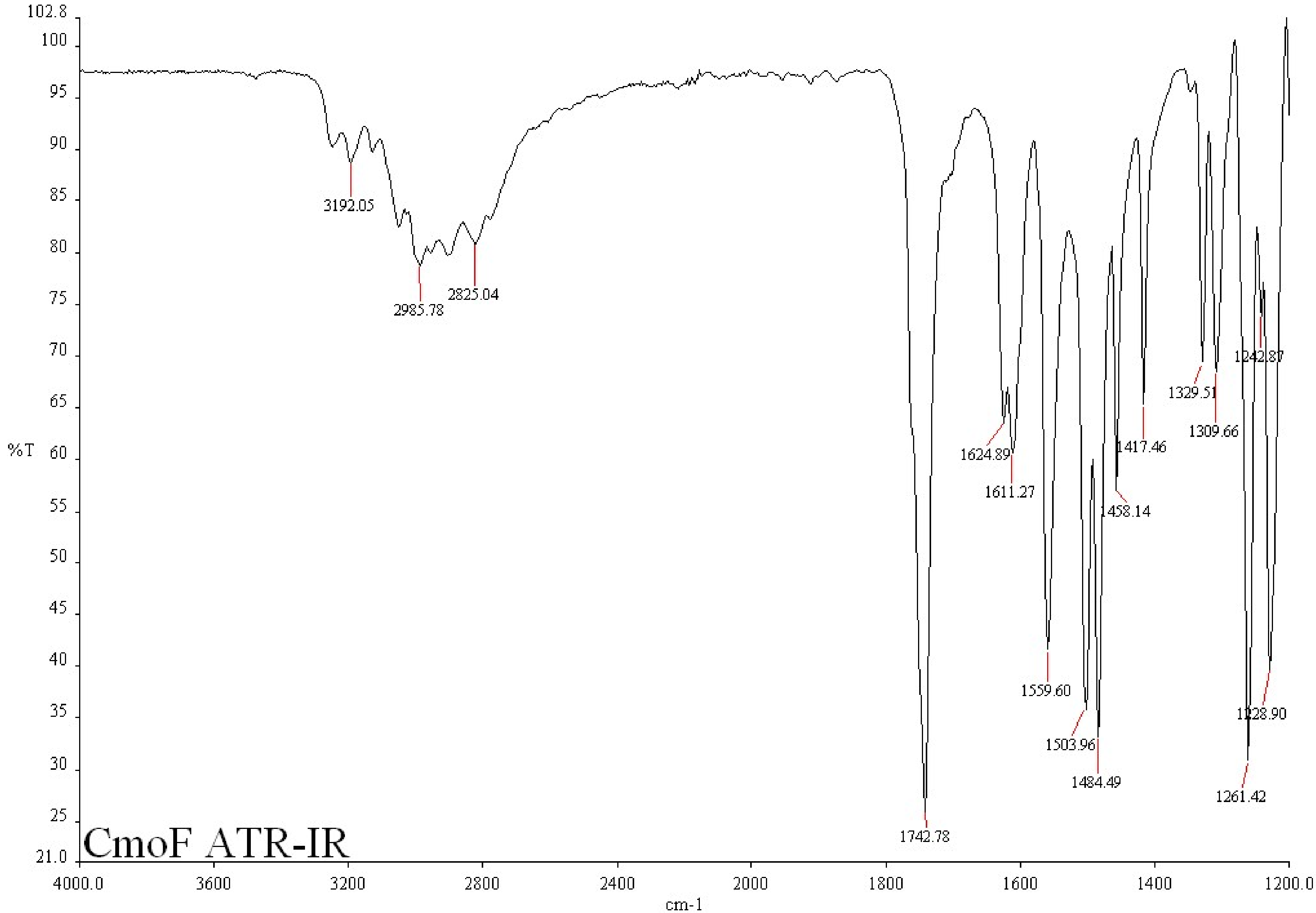
1.1.4.4. **CmpF**: 3178 (w), 3124 (w), 3080 (w), 2930 (w), 2822 (w), 1740 (s), 1602 (m), 1588 (s), 1563 (m), 1504 (s), 1477 (m), 1427 (s).



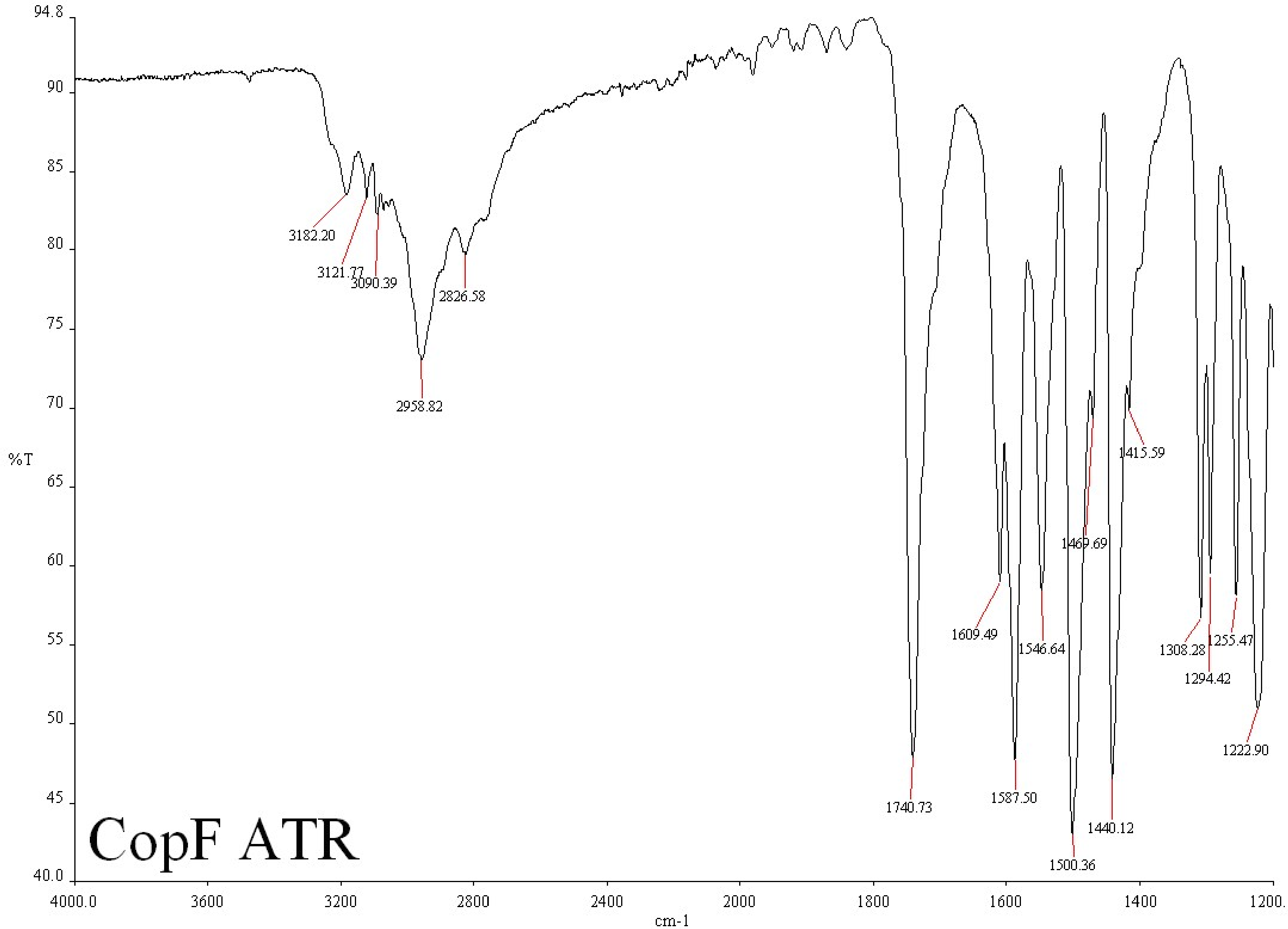
1.1.4.5. **CmmF**: 3180 (w), 2811 (m), 1745 (s), 1606 (s), 1588 (s), 1559 (m), 1486 (s), 1450 (m), 1425 (s).



1.1.4.6. **CmoF**: 3192 (w), 2986 (m), 2825 (m), 1743 (s), 1625 (m), 1611 (m), 1560 (s), 1504 (s), 1484 (s), 1458 (m), 1417 (m).



1.1.4.7. **CopF**: 3182 (w), 3122 (w), 3090 (w), 2959 (m), 2827 (w), 1741 (s), 1609 (s), 1587 (s), 1547 (s), 1500 (s), 1470 (m), 1440 (s), 1416 (m);

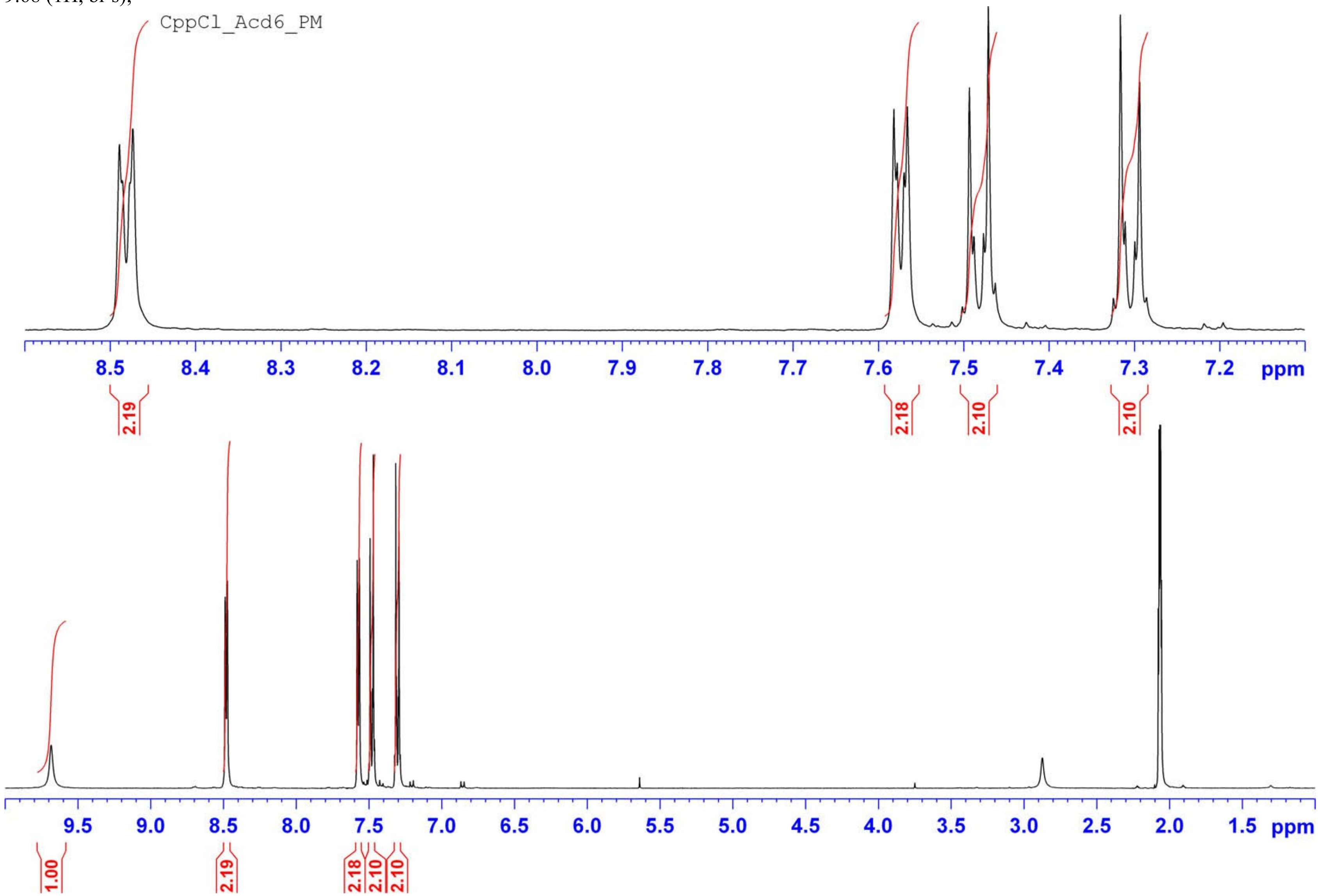


1.2. **CxxCl isomer grid**

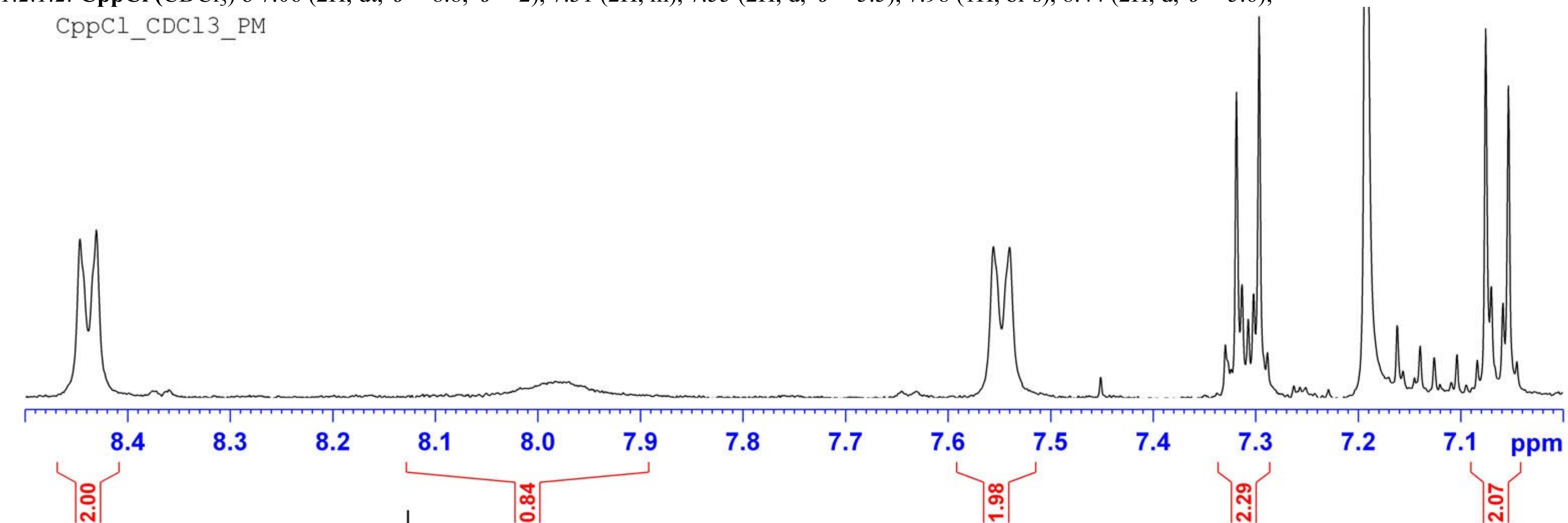
^1H NMR data	**pages 39-56**	(run in CD_3COCD_3, acetone-d_6 and $CDCl_3$)
^{13}C NMR data	**pages 57-65**	
Infra-red data	**pages 66-74**	

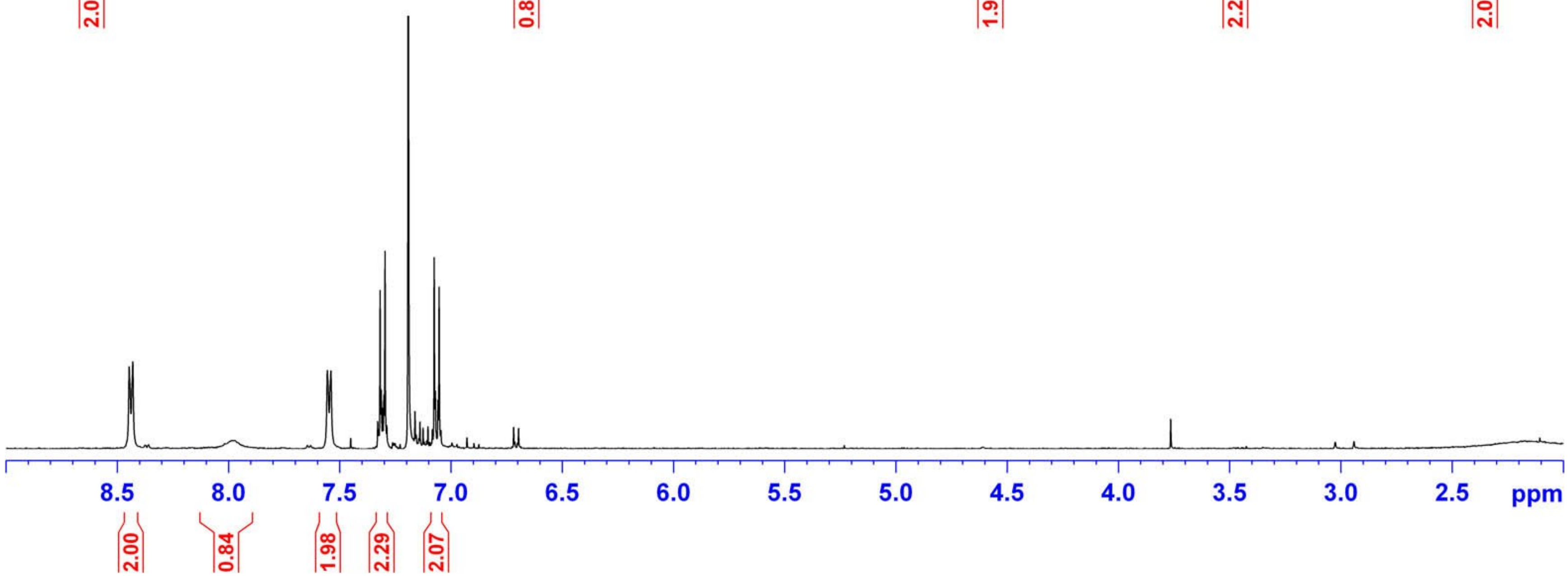
1.2.1. ^{1}H NMR data and spectra (400 MHz)

1.2.1.1. **CppCl** (Acetone-d_6): δ 7.30 (2H, dt, ^{3}J = 8.8, ^{4}J = 2.2), 7.48 (2H, dt, ^{3}J = 8.8, ^{4}J = 2.3), 7.57 (2H, dd, ^{3}J = 4.5, ^{4}J = 1.5), 8.48 (2H, dd, ^{3}J = 4.5, ^{4}J = 1.3); 9.68 (1H, br s);

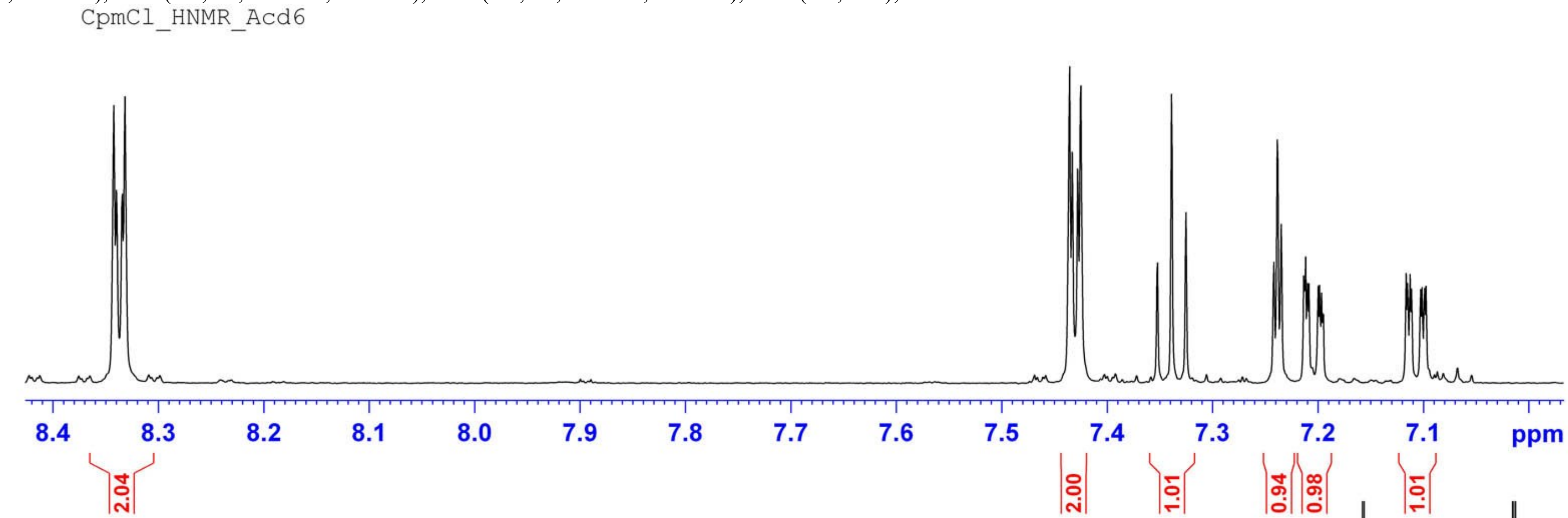


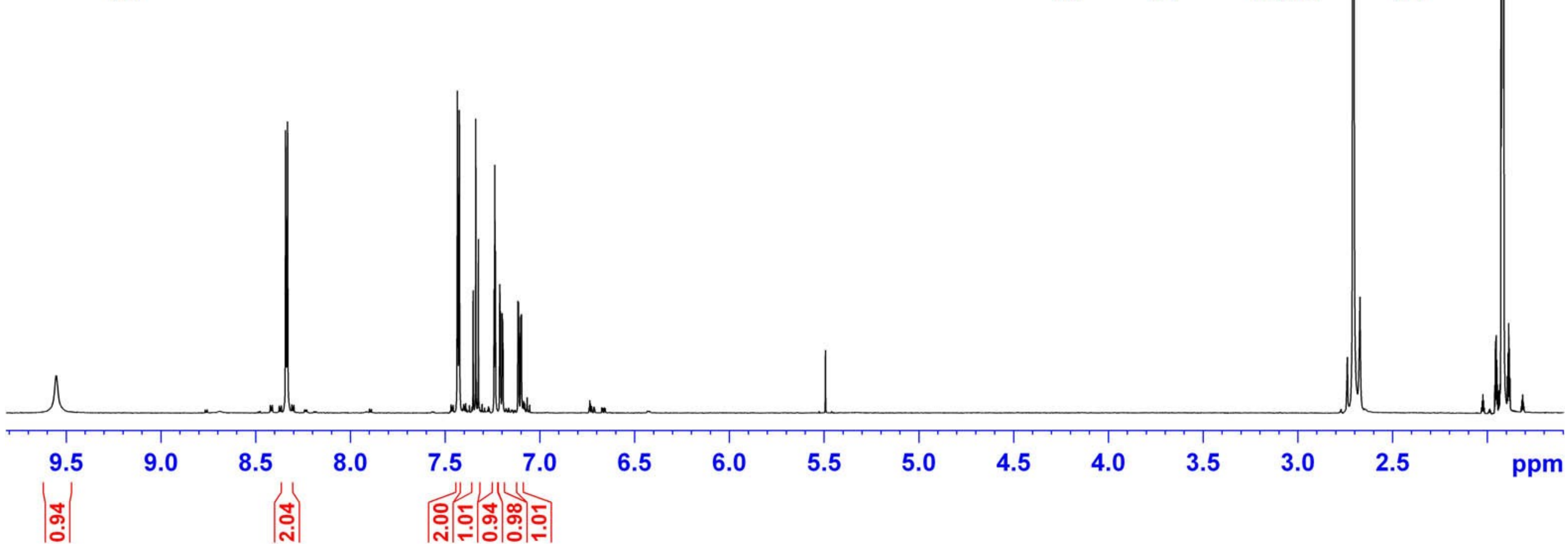
1.2.1.2. **CppCl (**$CDCl_3$) δ 7.06 (2H, dt, ^3J = 8.8, ^4J = 2), 7.31 (2H, m), 7.55 (2H, d, ^3J = 5.5), 7.98 (1H, br s), 8.44 (2H, d, ^3J = 5.6);



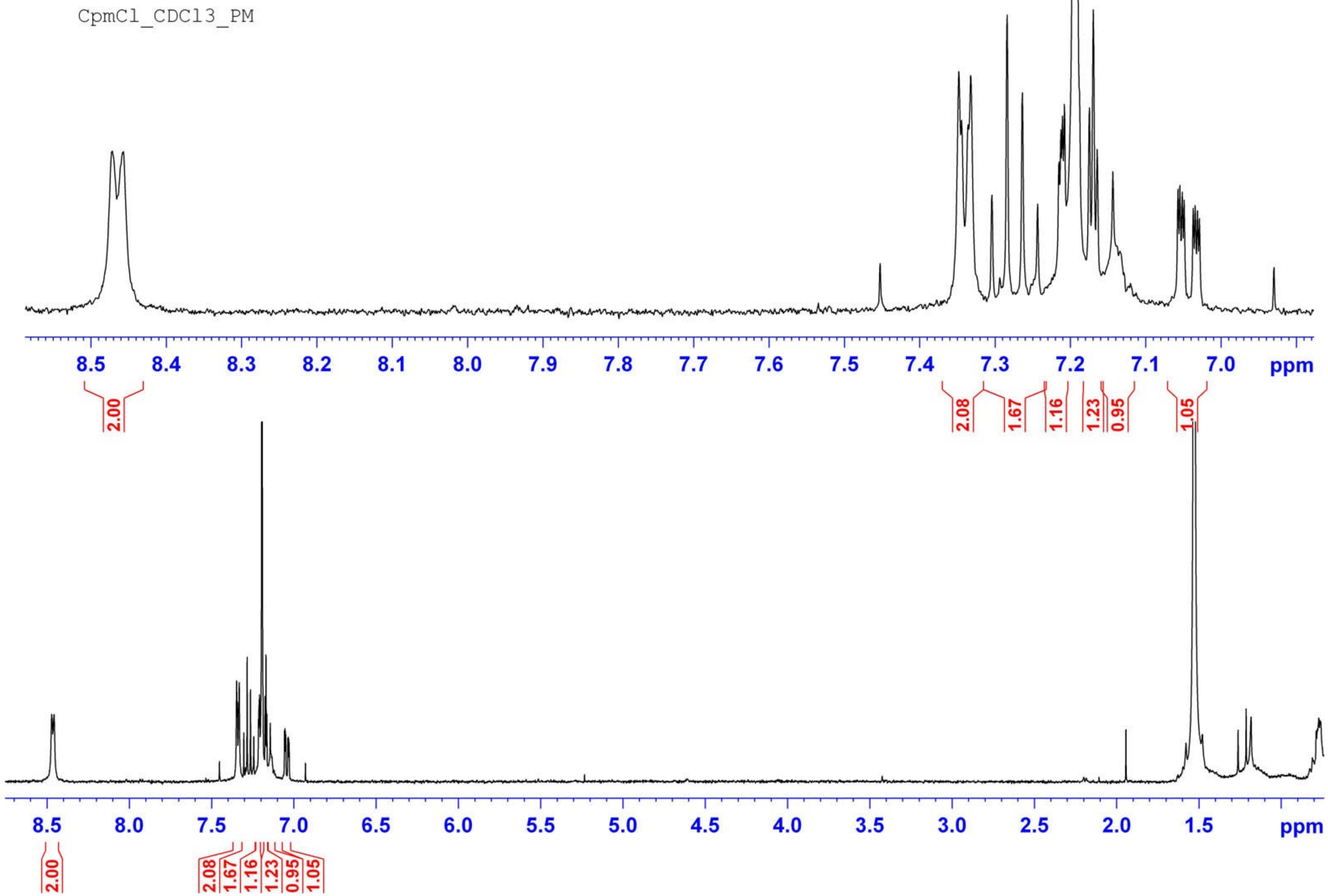


1.2.1.3. **CpmCl** (600 MHz, Acetone-d_6): δ 7.11 (1H, ddd, ^3J = 8.3, ^4J = 2.2, ^5J = 0.8), 7.20 (1H, ddd, ^3J = 8.0, ^4J = 1.9, ^5J = 0.8), 7.24 (1H, t, ^3J = 2.1), 7.34 (1H, t, ^3J = 8.2), 7.43 (2H, dd, ^3J = 5.0, ^4J = 1.5), 8.34 (2H, dd, ^3J = 4.8, ^4J = 1.4), 9.55 (1H, br s);

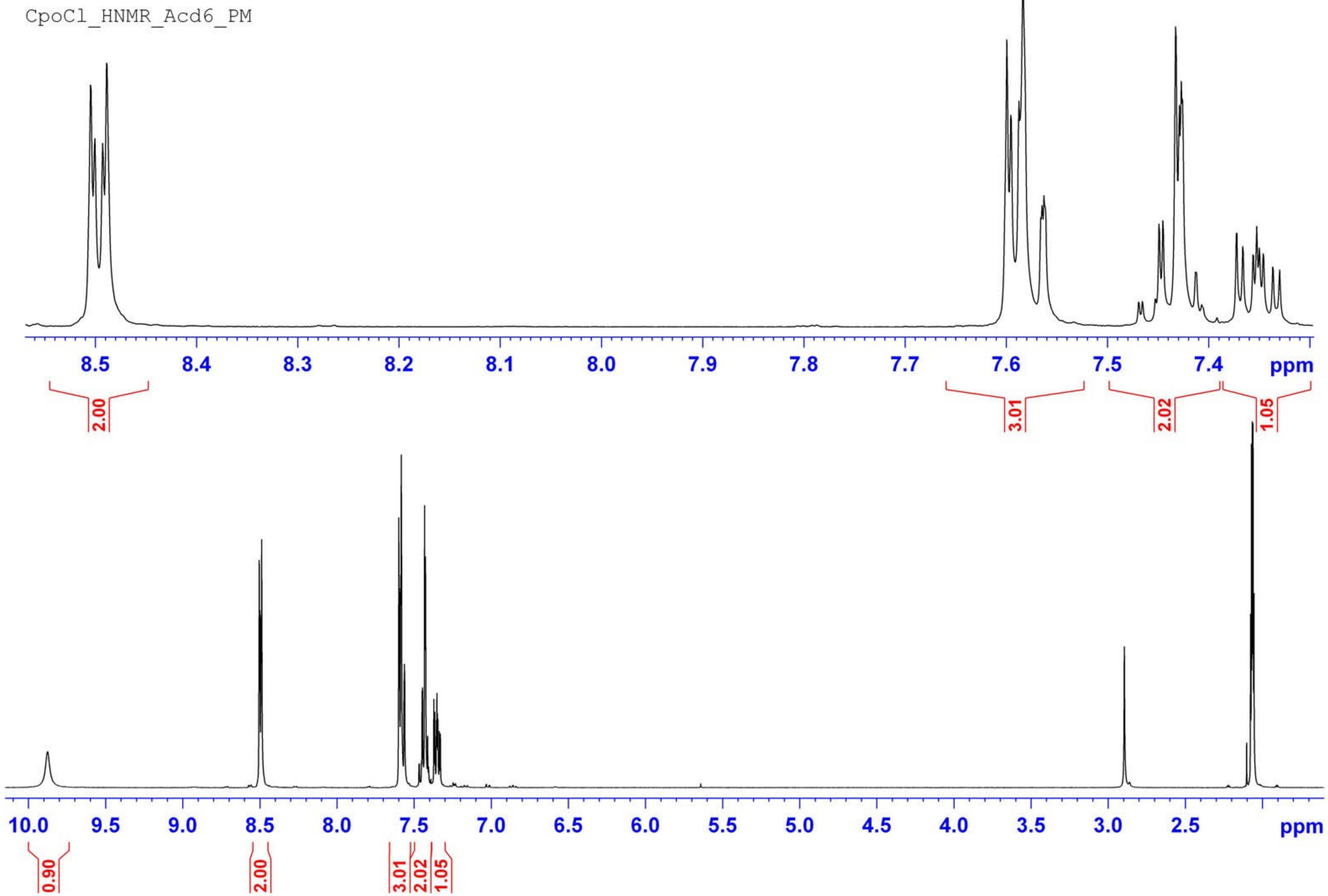




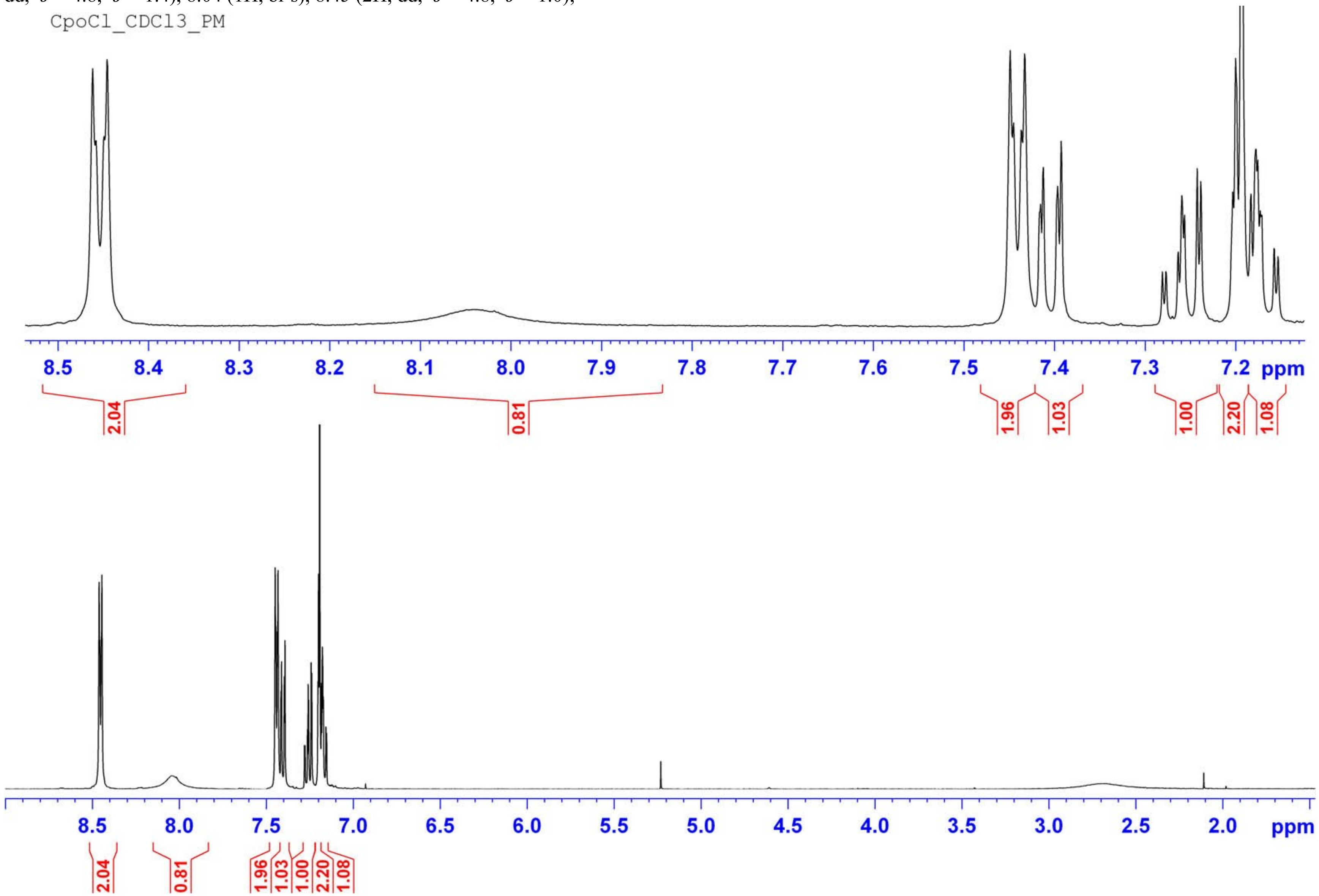
1.2.1.4. **CpmCl** ($CDCl_3$) δ 7.04 (1H, ddd, ^3J = 8.1, ^4J = 2.3, ^5J = 1.0), [7.14 (1H, br s), 7.17 (1H, t, ^3J = 2.0), 7.21 (1H, ddd, ^3J = 8.0, ^4J = 1.9, ^5J = 1.1), 7.28 (1H, t, ^3J = 8.1) includes residual $CHCl_3$ solvent], 7.34 (2H, dd, ^3J = 4.5, ^4J = 1.5), 8.46 (2H, d, ^3J = 5.7); (Refer to previous page for the acetone-d_6 spectrum)



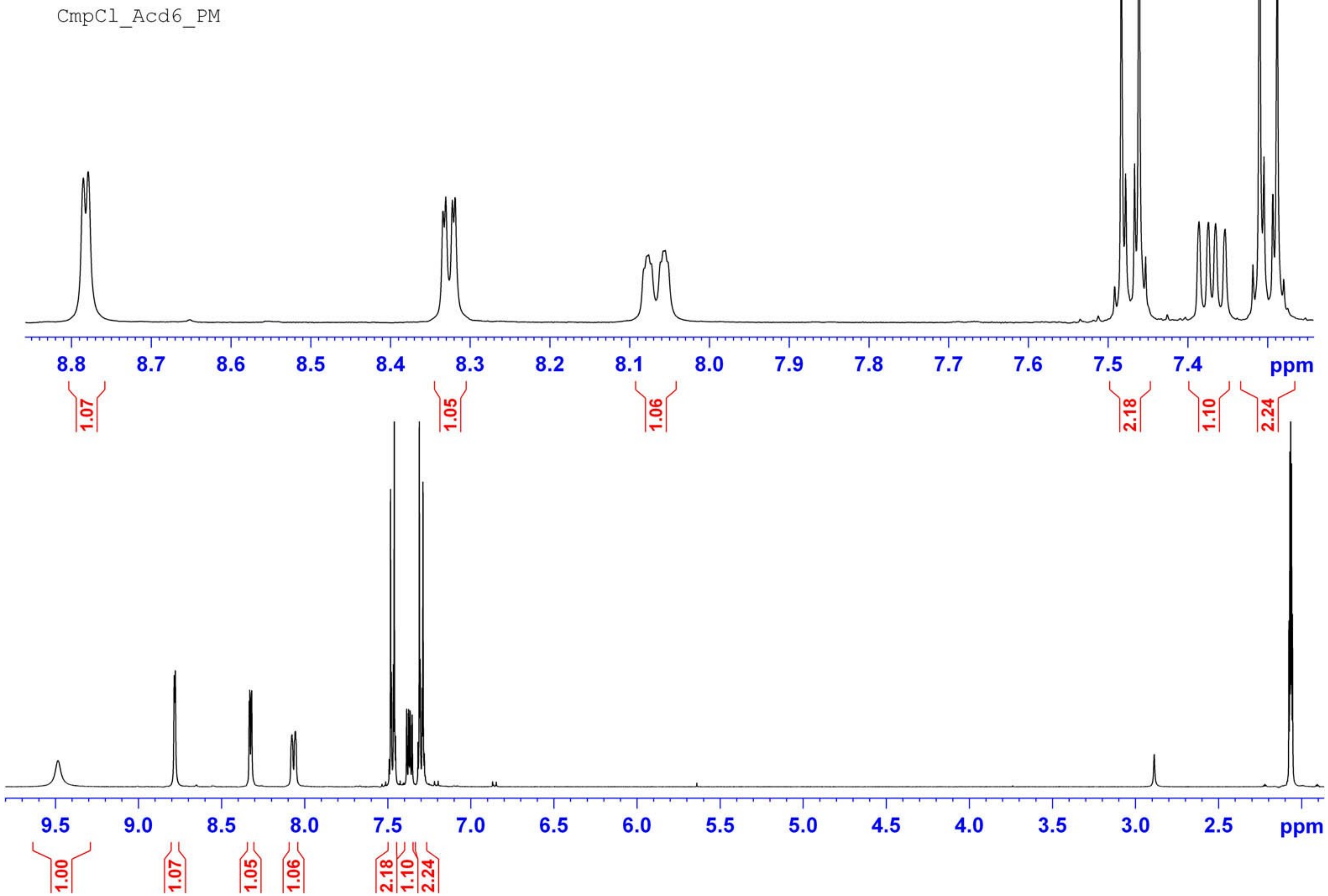
1.2.1.5. **CpoCl** (Acetone-d_6): δ 7.35 (1H, ddd, ^3J = 8.0, ^4J = 6.6, ^5J = 2.5), 7.43 (2H, m), 7.57 (1H, dd, ^3J = 8.0, ^4J = 1.0), 7.59 (2H, dd, ^3J = 5.2, ^4J = 1.6), 8.5 (2H, dd, ^3J = 4.8, ^4J = 1.5), 9.88 (1H, br s);



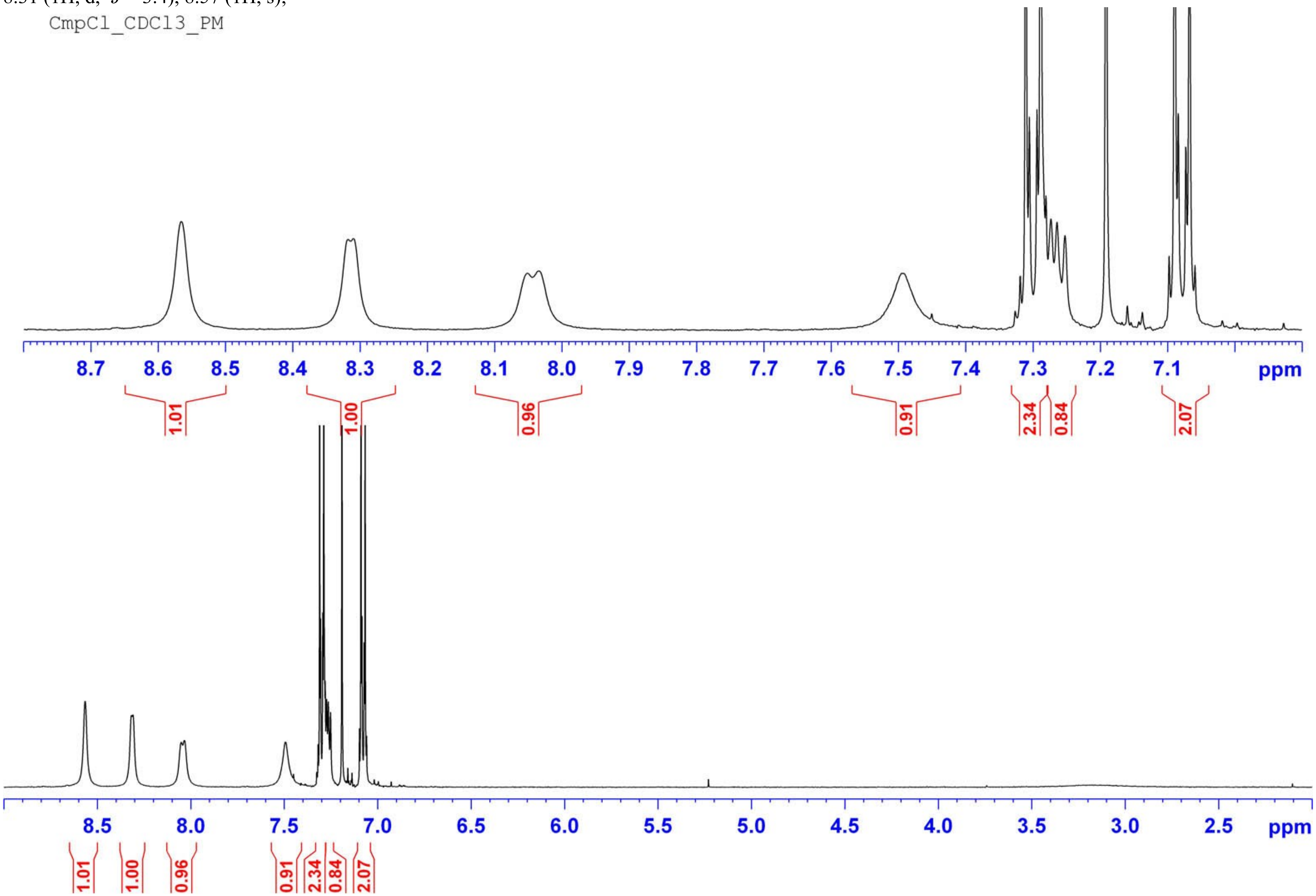
1.2.1.6. **CpoCl** ($CDCl_3$) δ 7.19 (2H, m), 7.26 (1H, ddd, ^3J = 8.8, ^4J = 7.0, ^5J = 1.6; includes residual $CHCl_3$ solvent), 7.40 (1H, dd, ^3J = 7.7, ^4J = 1.6), 7.44 (2H, dd, ^3J = 4.8, ^4J = 1.4), 8.04 (1H, br s), 8.45 (2H, dd, ^3J = 4.8, ^4J = 1.0);



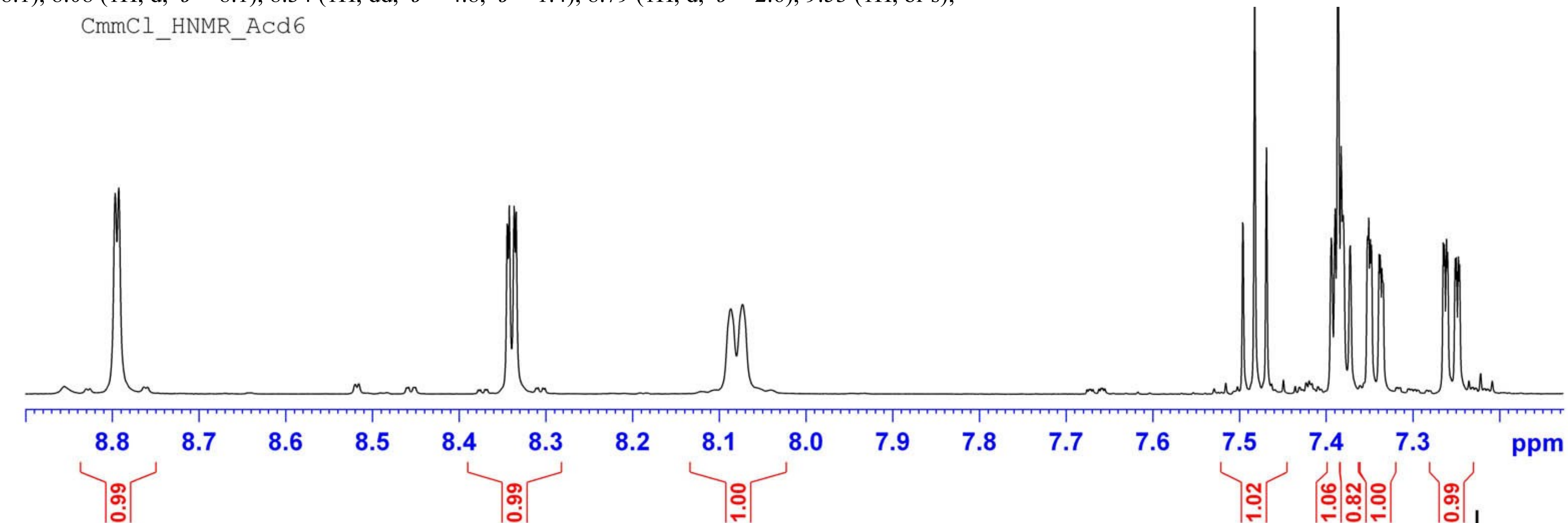
1.2.1.7. **CmpCl** (Acetone-d_6): δ 7.30 (2H, dt, ^3J = 8.9, ^4J = 2.7), 7.37 (1H, dd, ^3J = 8.4, ^4J = 4.7), 7.47 (2H, dt, ^3J = 9.0, ^4J = 2.8), 8.07 (1H, ddd, ^3J = 8.3, ^4J = 3, ^5J =1.4), 8.33 (1H, dd, ^3J = 4.7, ^4J = 1.4), 8.78 (1H, d, ^3J = 2.5), 9.48 (1H, br s);

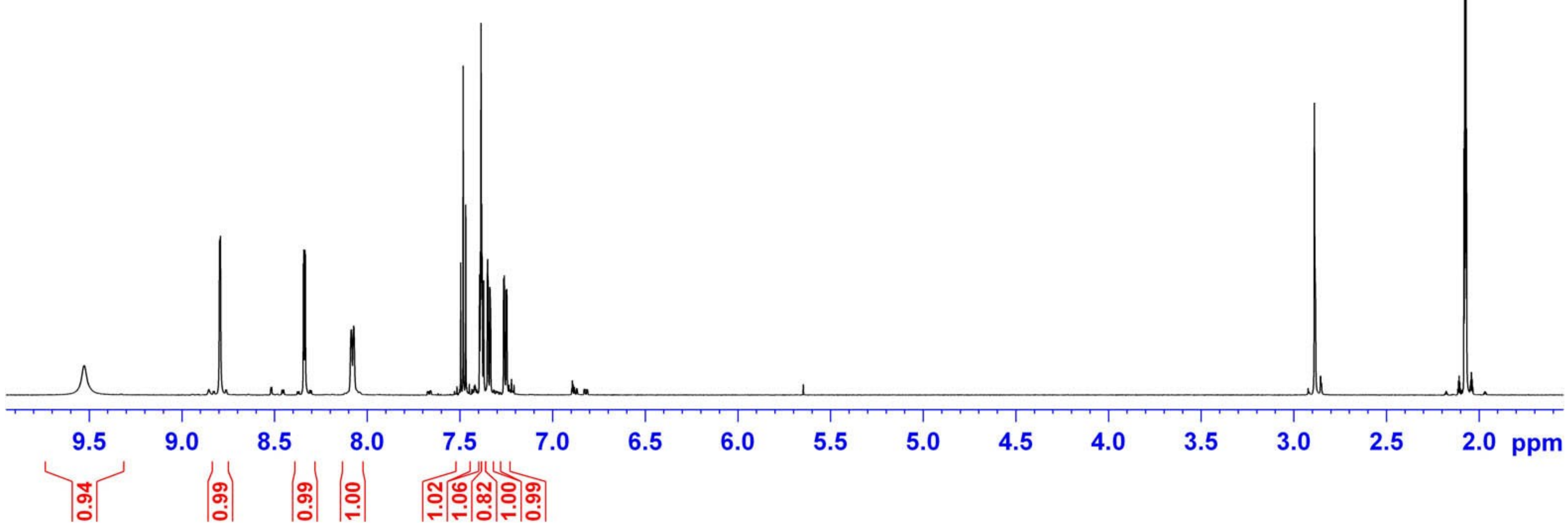


1.2.1.8. **CmpCl** ($CDCl_3$) δ 7.08 (2H, dt, ^3J = 8.9, ^4J = 2.7), 7.27 (1H, dd, ^3J = 8.2, ^4J = 4.8), 7.30 (2H, dt, ^3J = 8.9, ^4J = 2.7), 7.49 (1H, br s), 8.04 (1H, d, ^3J = 7), 8.31 (1H, d, ^3J = 3.4), 8.57 (1H, s);

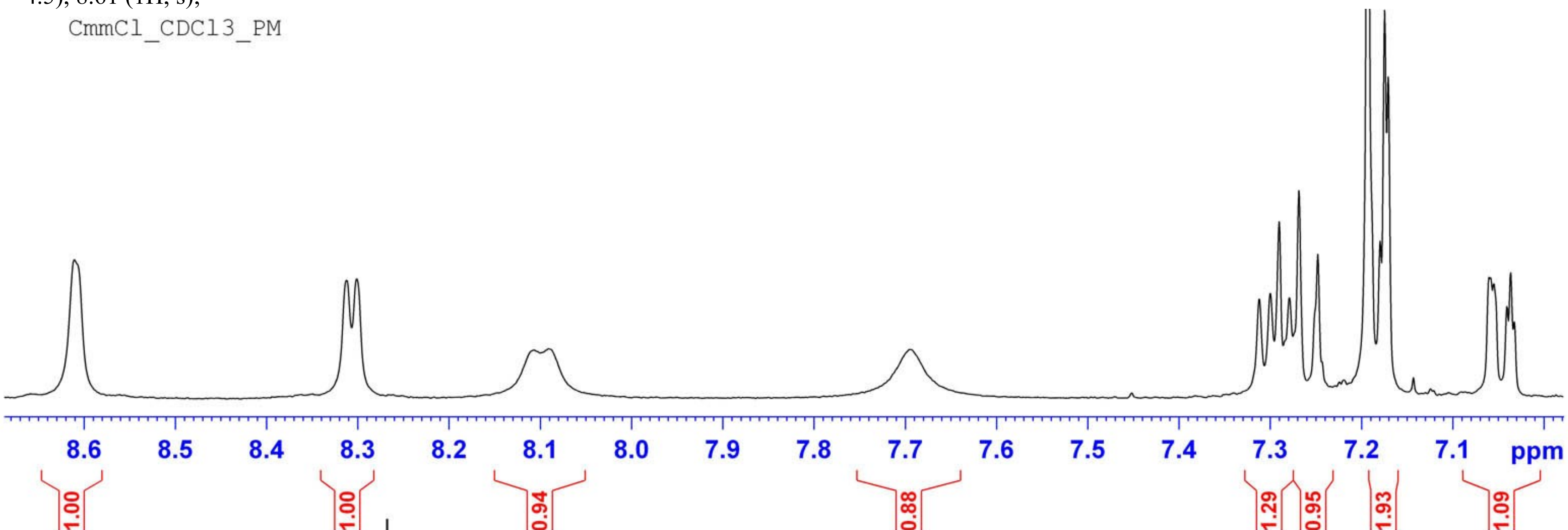


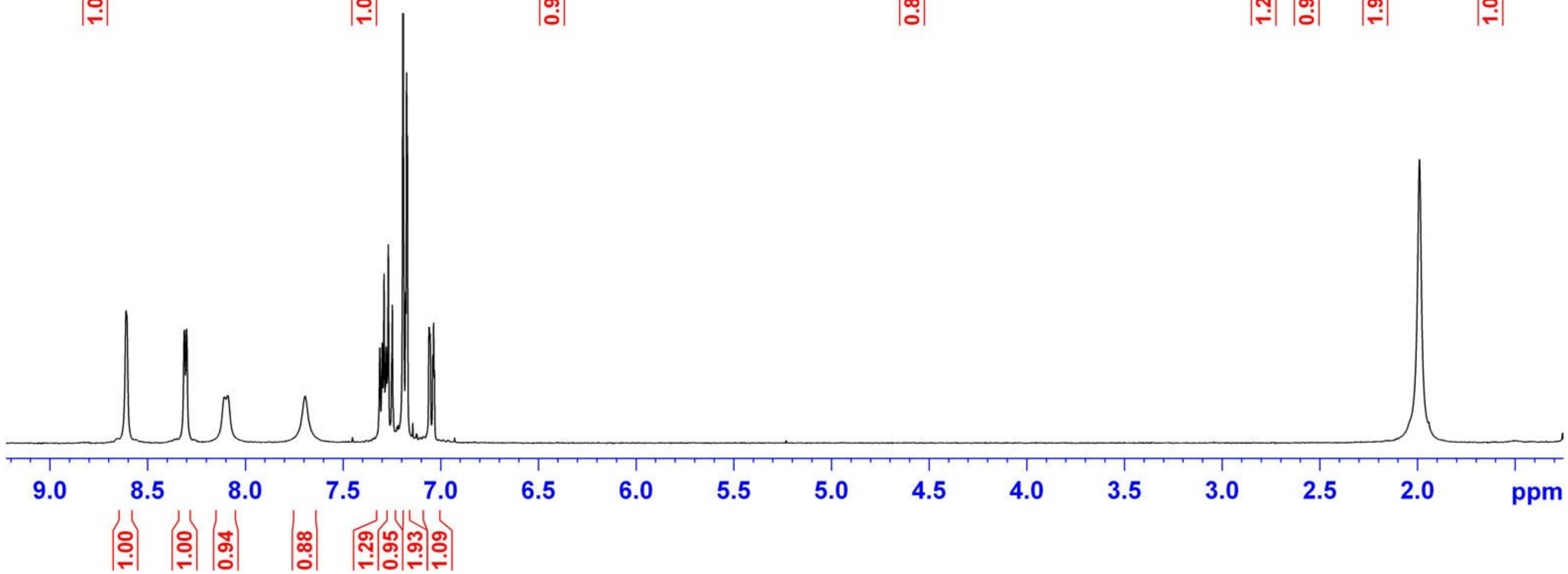
1.2.1.9. **CmmCl** (600 MHz, Acetone-d_6): δ 7.25 (1H, ddd, ${}^3J$ = 8.3, ${}^4J$ = 2.2, ${}^5J$ = 0.8), 7.34 (1H, ddd, ${}^3J$ = 8.2, ${}^4J$ = 1.8, ${}^5J$ = 0.8), 7.38 (2H, m), 7.48 (1H, t, ${}^3J$ = 8.1), 8.08 (1H, d, ${}^3J$ = 8.1), 8.34 (1H, dd, ${}^3J$ = 4.8, ${}^4J$ = 1.4), 8.79 (1H, d, ${}^3J$ = 2.6), 9.53 (1H, br s);



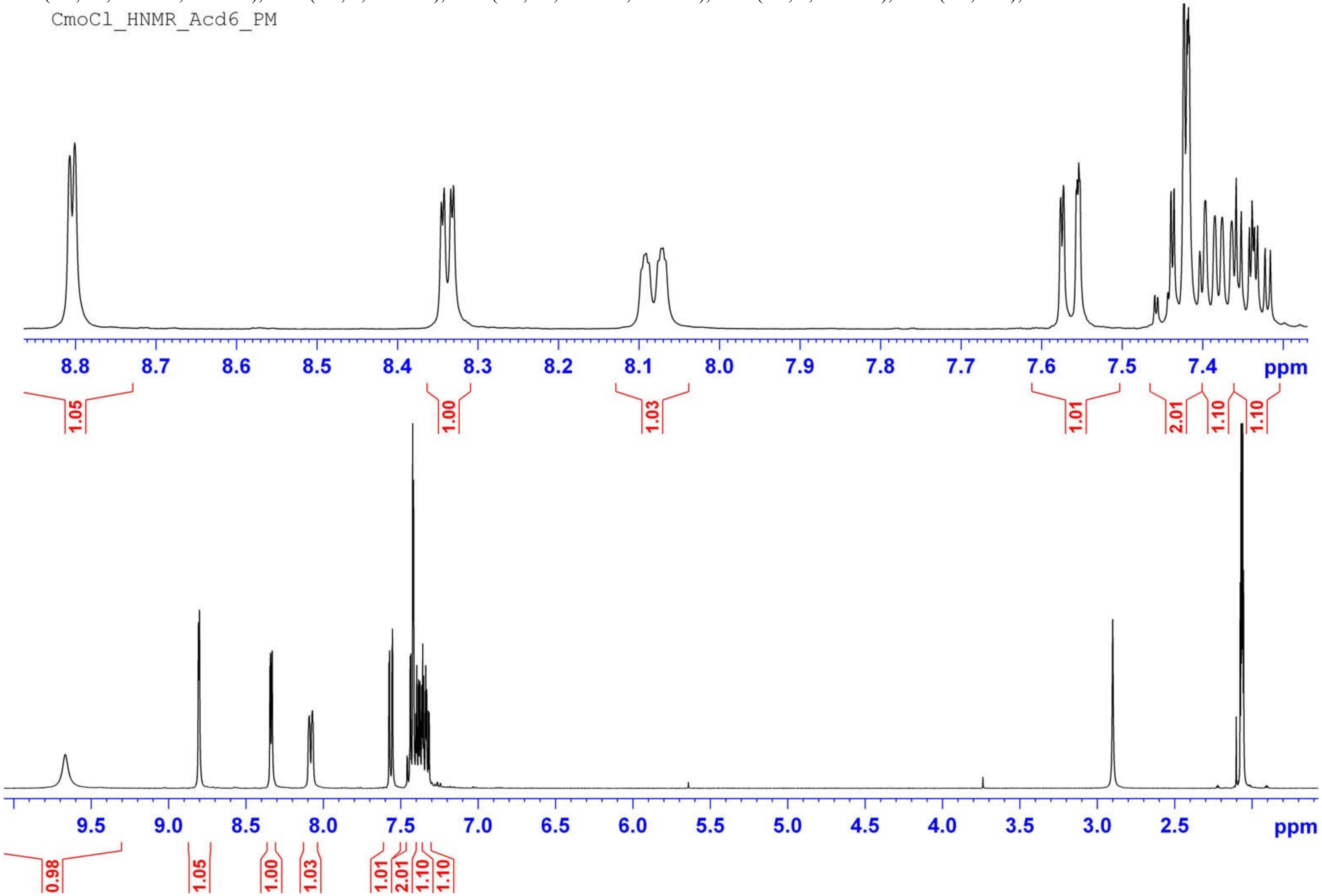


1.2.1.10. **CmmCl** ($CDCl_3$) δ 7.05 (1H, dt, ^{3}J = 8.1, ^{4}J = 1.8), 7.18 (2H, m), 7.27 (1H, t, ^{3}J = 8.2), 7.29 (1H, m), 7.69 (1H, br s), 8.10 (1H, d, ^{3}J = 6.9), 8.3 (1H, d, ^{3}J = 4.5), 8.61 (1H, s);

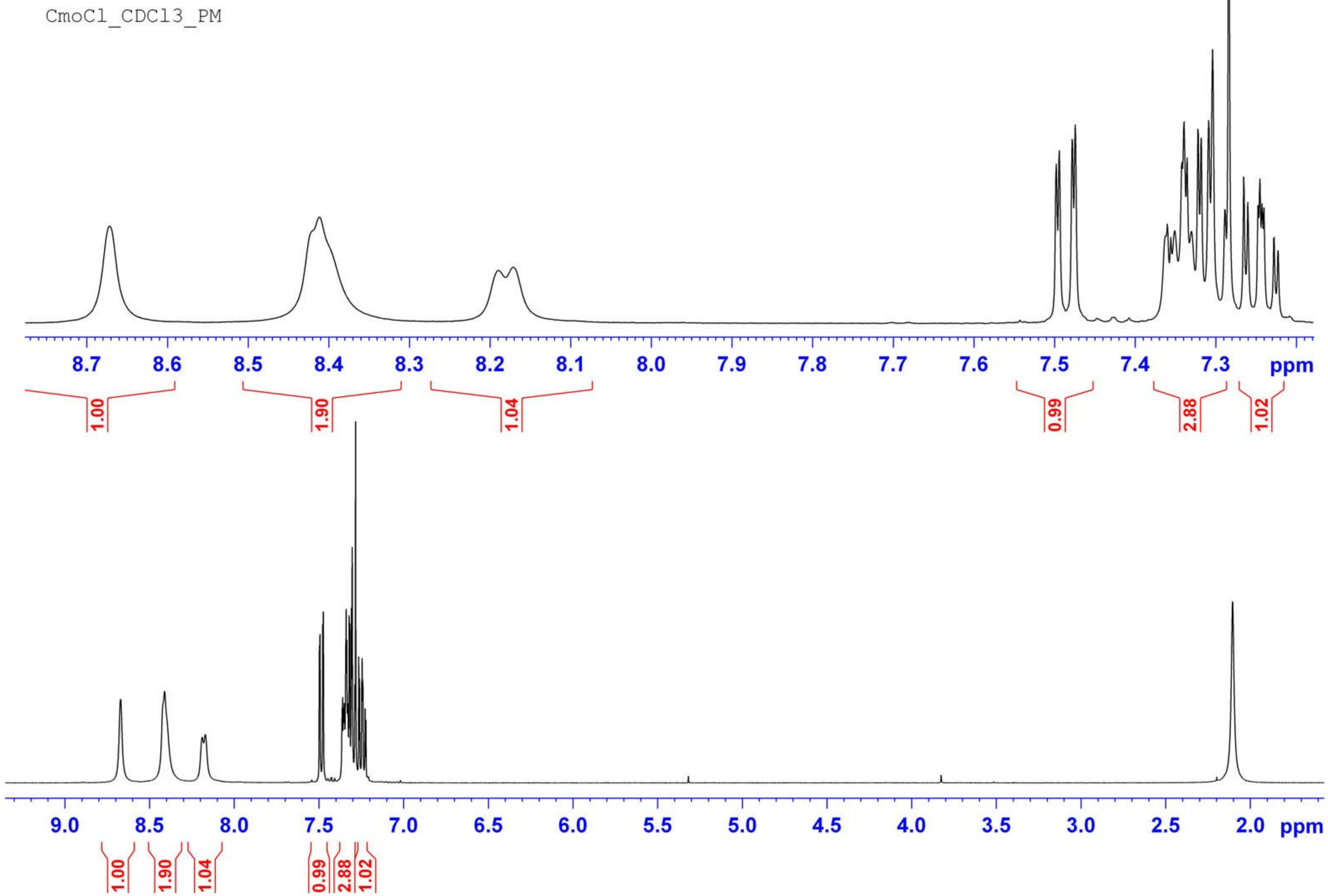




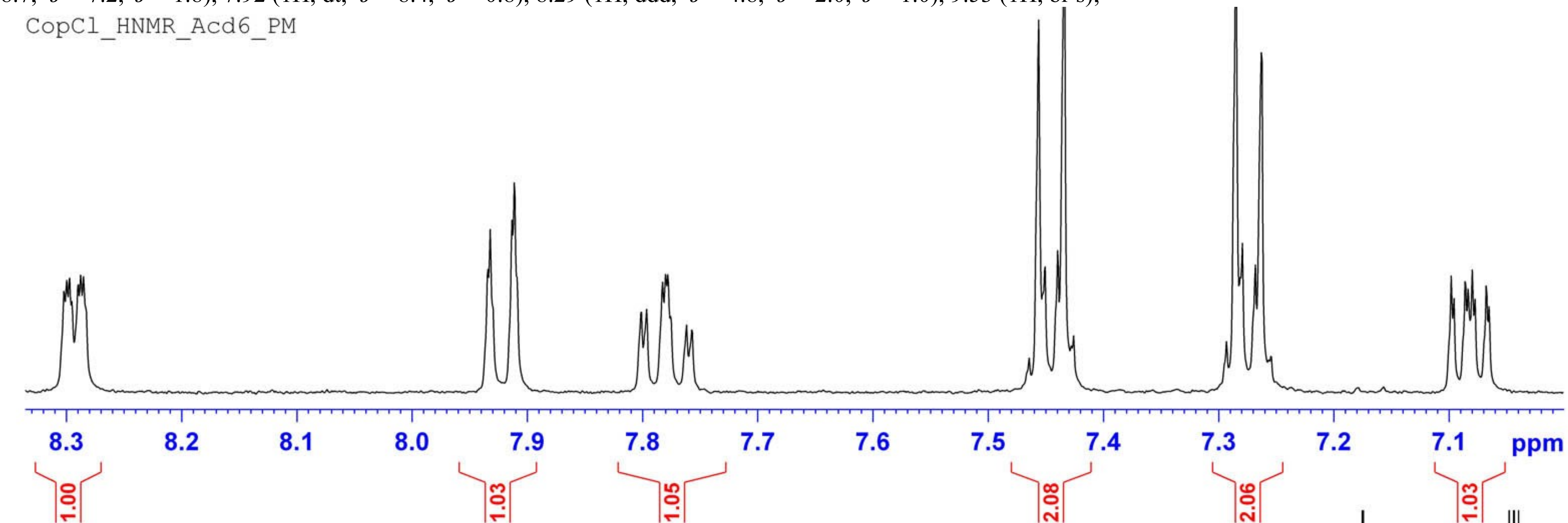
1.2.1.11. **CmoCl** (Acetone-d_6): δ 7.34 (1H, ddd, ^3J = 8.2, ^4J = 6.6, ^5J = 2.5), 7.38 (1H, dd, ^3J = 8.5, ^4J = 4.7) 7.42 (1H, d, ^3J = 2.2), 7.44 (1H, td, ^3J = 8.0, ^4J = 1.7) 7.56 (1H, dd, ^3J = 8.0, ^4J = 1.4), 8.08 (1H, d, ^3J = 8.2), 8.34 (1H, dd, ^3J = 4.6, ^4J = 1.3), 8.80 (1H, d, ^3J = 2.5), 9.67 (1H, br s);

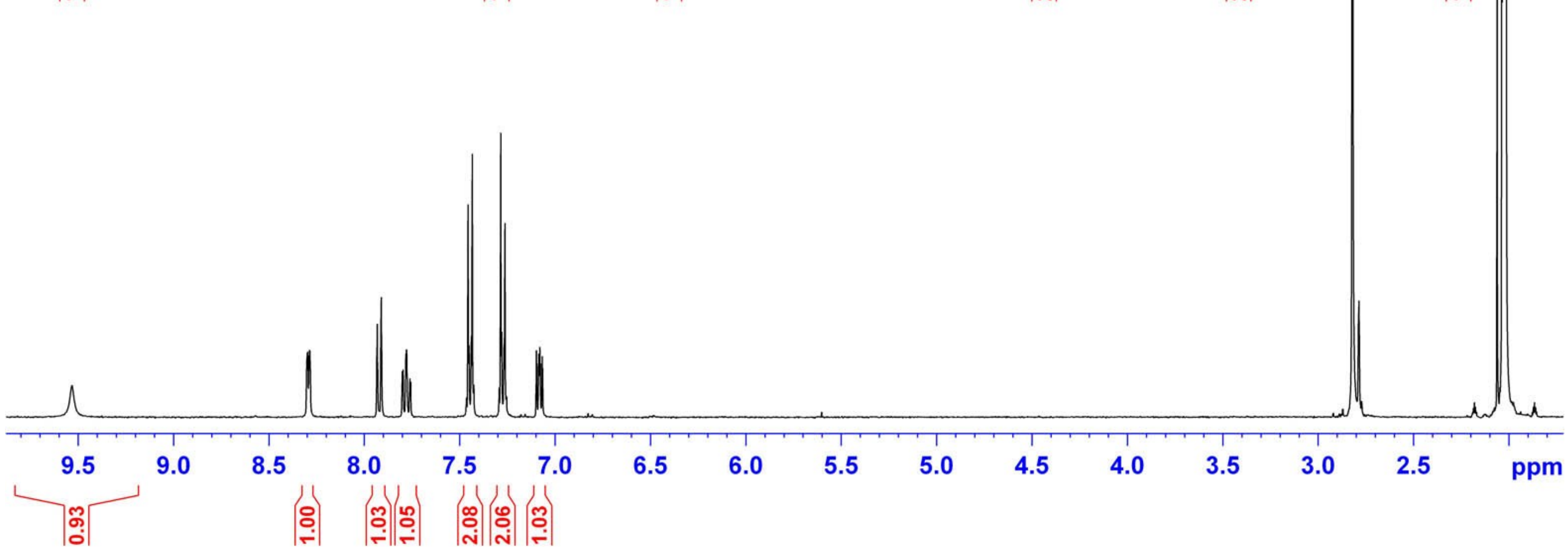


1.2.1.12. **CmoCl** ($CDCl_3$) δ δ 7.24 (1H, ddd, ^{3}J = 8.0, ^{4}J = 7.0, ^{5}J = 2.0), 7.29 (1H, m), 7.34 (2H, m), 7.49 (1H, dd, ^{3}J = 7.9, ^{4}J = 1.4), 8.18 (1H, d, ^{3}J = 7.3), 8.40 (1H, br s), 8.42 (1H, d, ^{3}J = 3.5), 8.67 (1H, s);

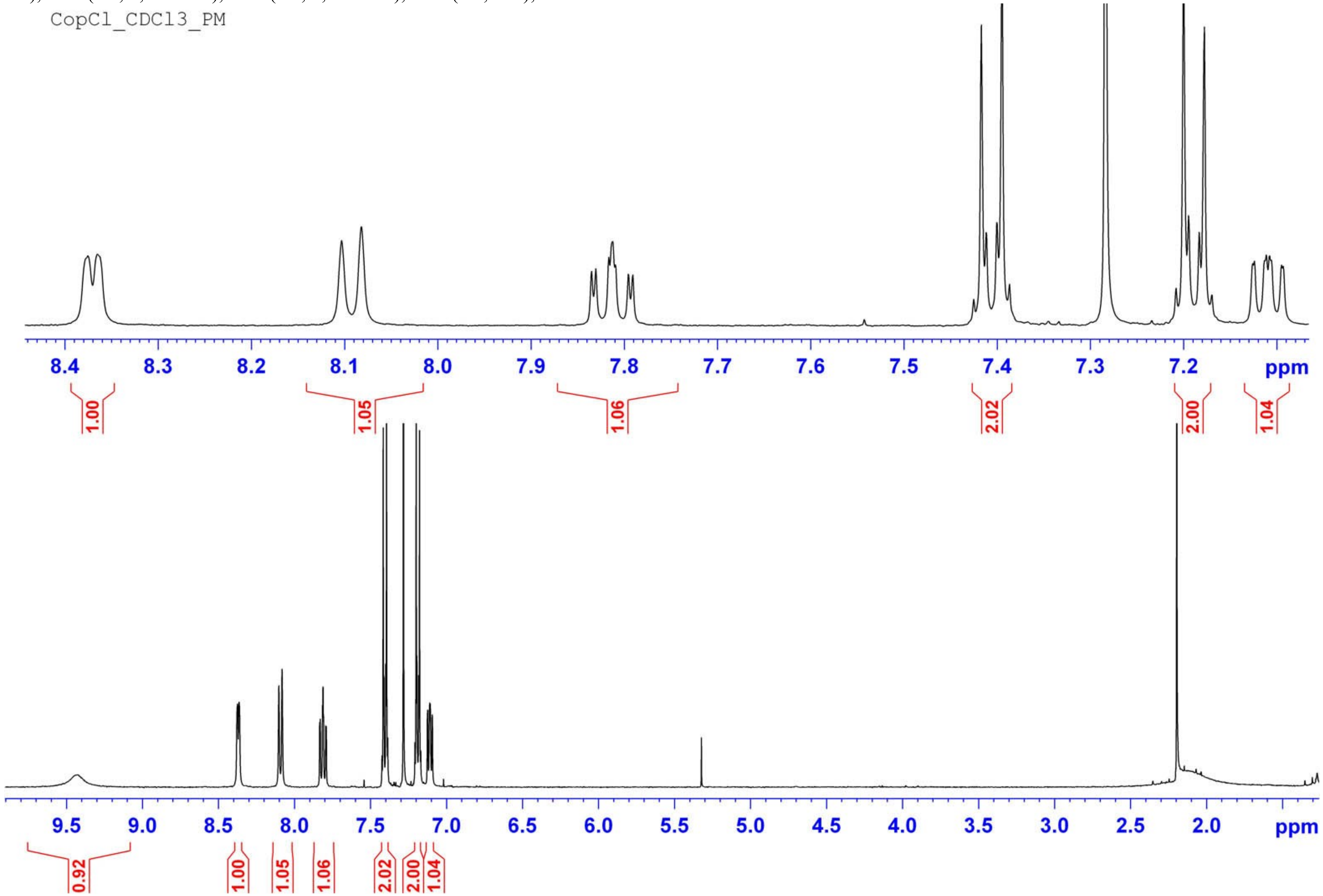


1.2.1.13. **CopCl** (Acetone-d_6): δ 7.08 (1H, ddd, ^{3}J = 7.4, ^{4}J = 4.9, ^{5}J = 0.9), 7.27 (2H, dt, ^{3}J = 8.8, ^{4}J = 2.5), 7.44 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.5), 7.78 (1H, ddd, ^{3}J = 8.7, ^{4}J = 7.2, ^{5}J = 1.8), 7.92 (1H, dt, ^{3}J = 8.4, ^{4}J = 0.8), 8.29 (1H, ddd, ^{3}J = 4.8, ^{4}J = 2.0, ^{5}J = 1.0), 9.53 (1H, br s);

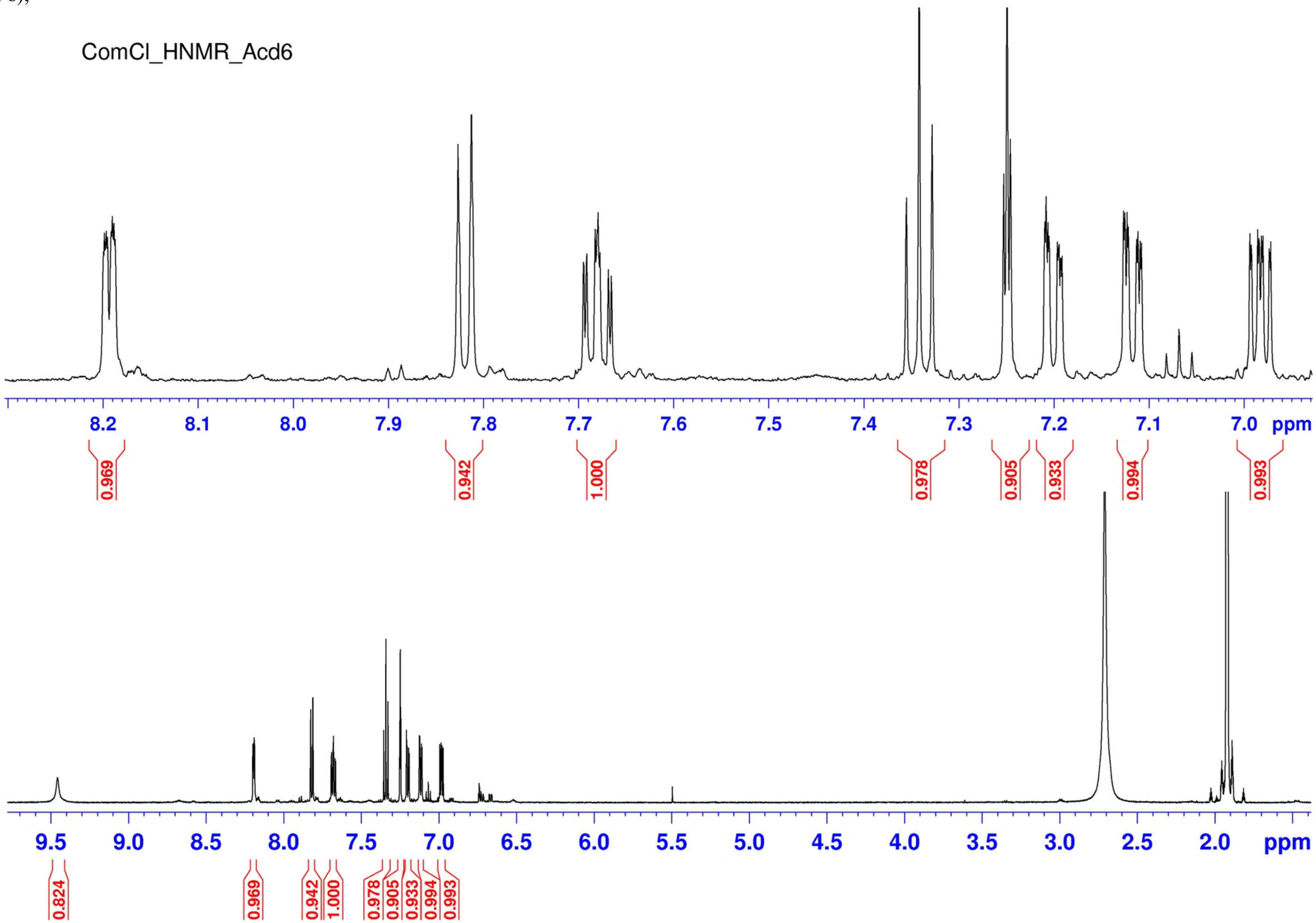




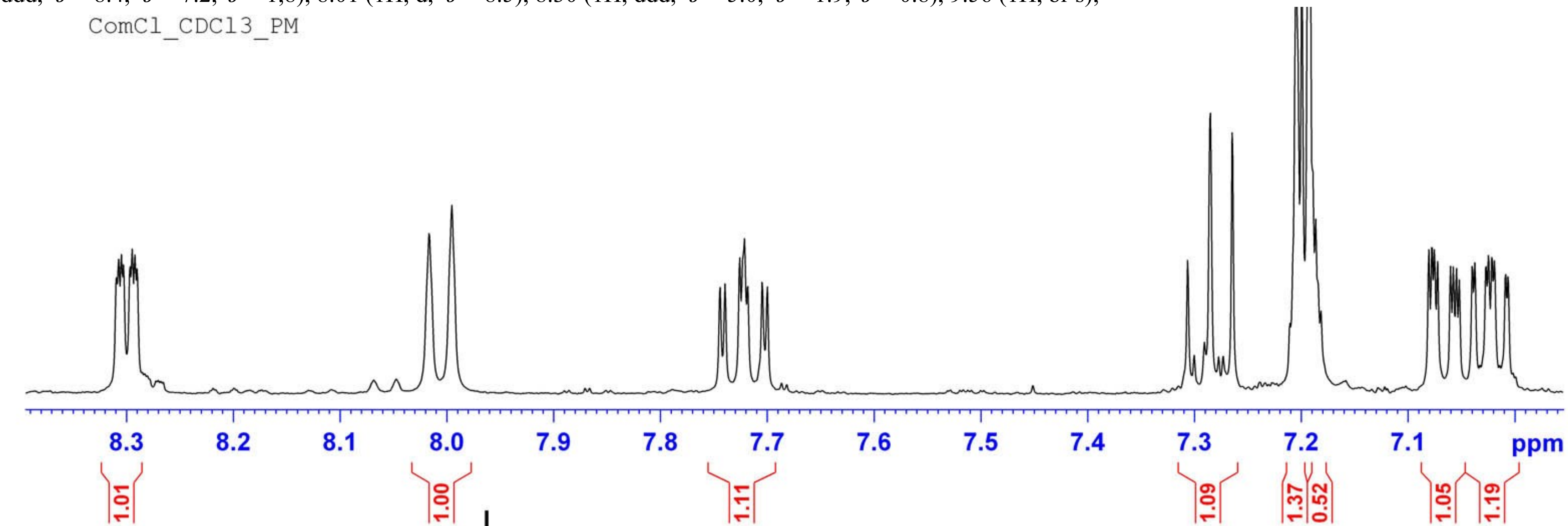
1.2.1.14. **CopCl** ($CDCl_3$) δ 7.11 (1H, ddd, ^3J = 7.7, ^4J = 5.2, ^5J = 0.8), 7.19 (2H, dt, ^3J = 8.9, ^4J = 2.5), 7.41 (2H, dt, ^3J = 8.8, ^4J = 2.5), 7.81 (1H, td, ^3J = 8.0, ^4J = 1.8), 8.09 (1H, d, ^3J = 8.5), 8.37 (1H, d, ^3J = 5.0), 9.43 (1H, br s);

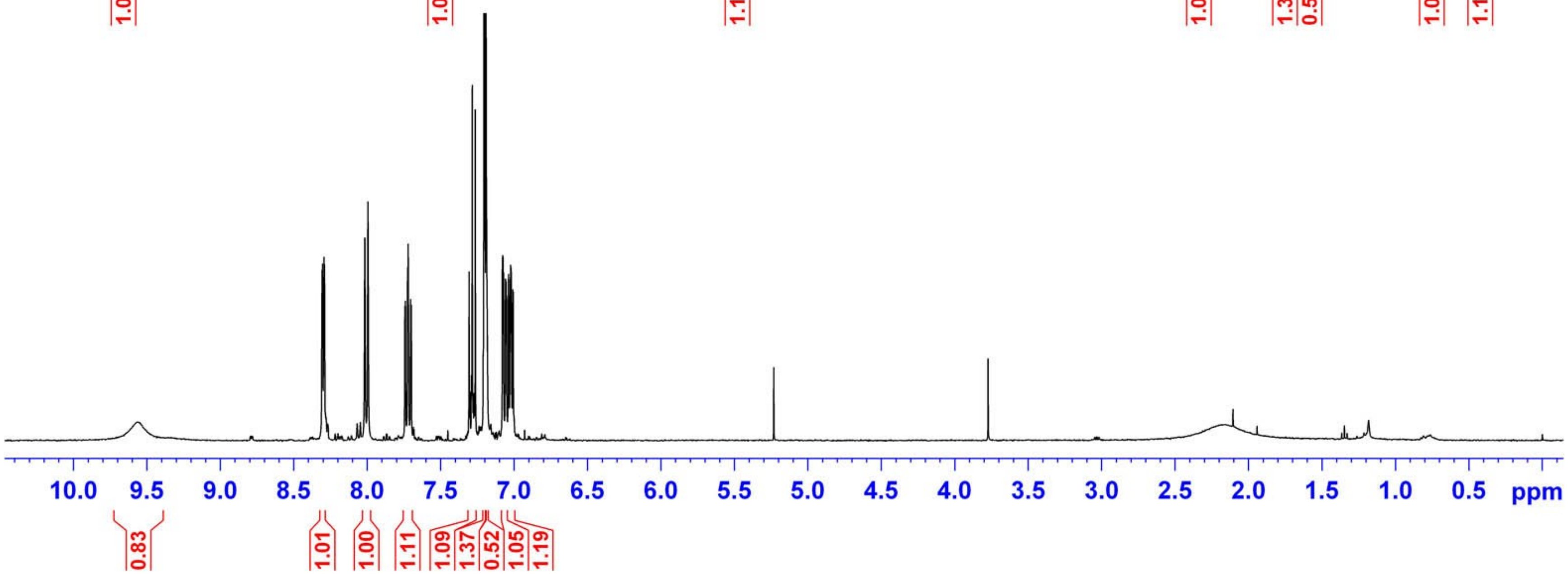


1.2.1.15. **ComCl** (Acetone-d_6): δ 6.98 (1H, ddd, ^3J = 7.7, ^4J = 4.9, ^5J = 0.9), 7.12 (1H, ddd, ^3J = 8.3, ^4J = 2.3, ^5J = 0.7), 7.20 (1H, ddd, ^3J = 7.9, ^4J = 1.9, ^5J = 0.8), 7.25 (1H, t, ^3J = 2.1), 7.34 (1H, t, ^3J = 8.3), 7.68 (1H, ddd, ^3J = 9.1, ^4J = 6.9, ^5J = 2.0), 7.82 (1H, d, ^3J = 8.3), 8.19 (1H, ddd, ^3J = 5.0, ^4J = 1.8, ^5J = 0.7), 9.46 (1H, br s);

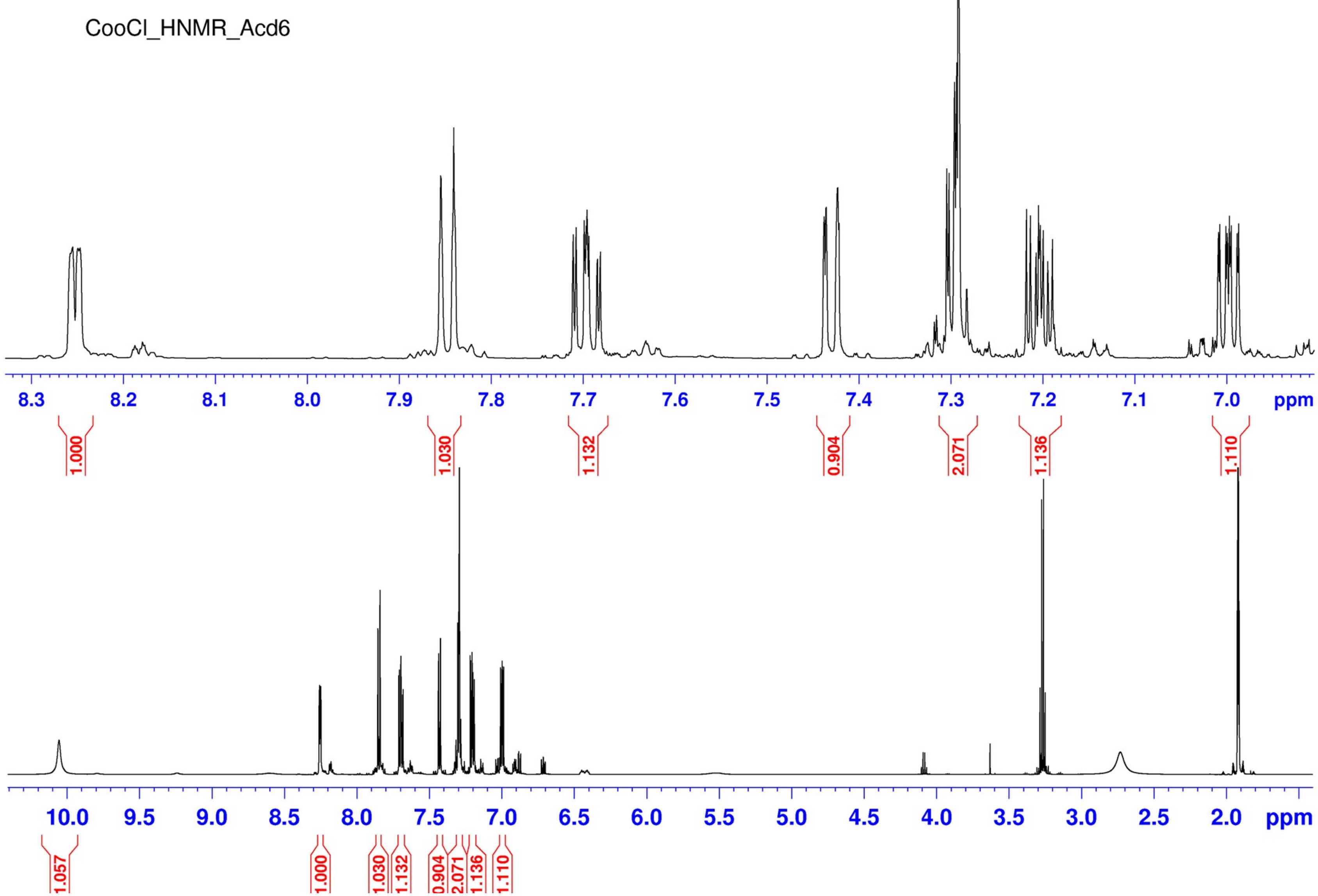


1.2.1.16. **ComCl** ($CDCl_3$) δ 7.02 (1H, ddd, ^3J = 7.5, ^4J = 5.1, ^5J = 0.9), 7.07 (1H, ddd, ^3J = 8.2, ^4J = 2.2, ^5J = 1.1) 7.20 (2H, m), 7.29 (1H, t, ^3J = 8.3), 7.72 (1H, ddd, ^3J = 8.4, ^4J = 7.2, ^5J = 1,8), 8.01 (1H, d, ^3J = 8.5), 8.30 (1H, ddd, ^3J = 5.0, ^4J = 1.9, ^5J = 0.8), 9.56 (1H, br s);

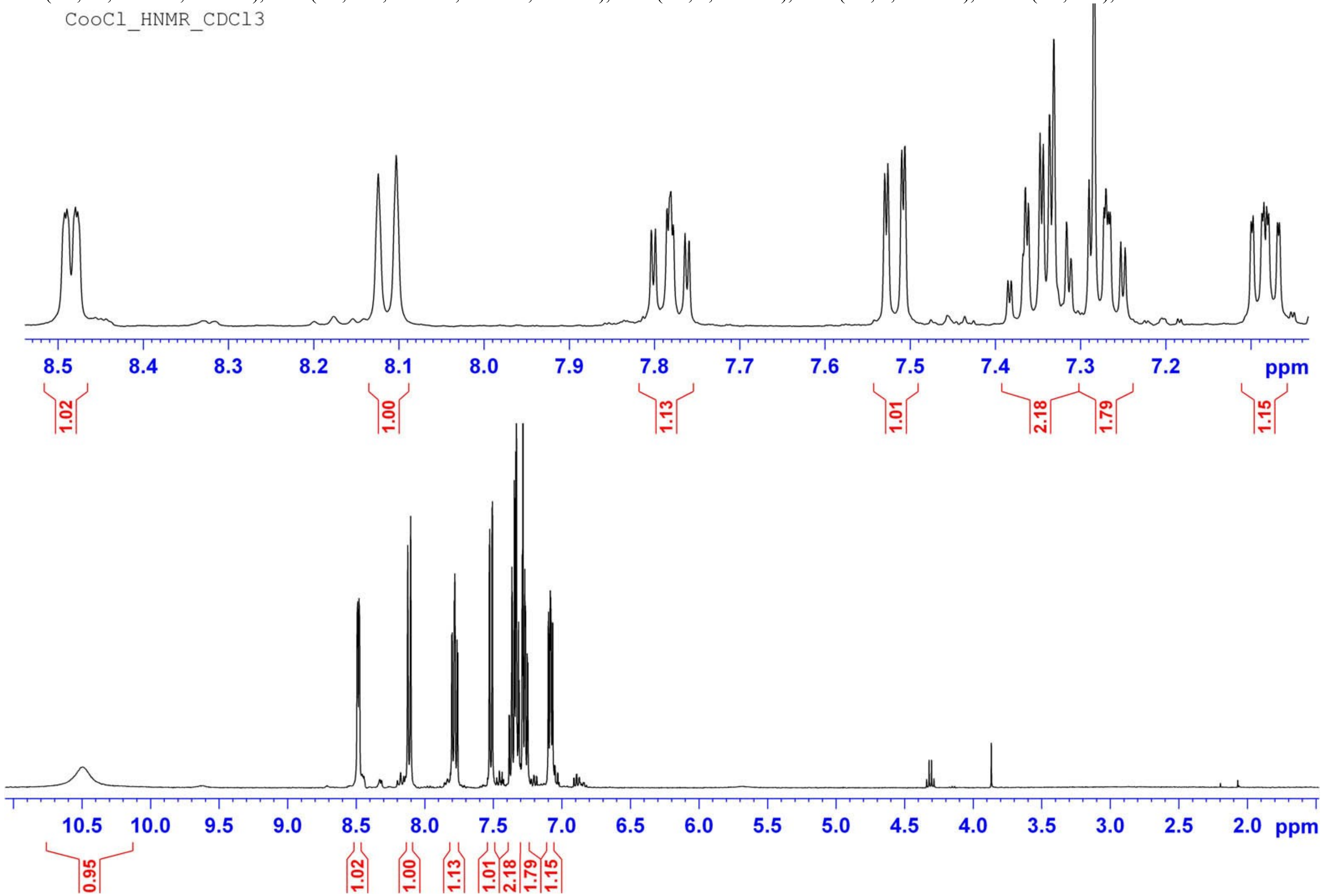




1.2.1.17. **CooCl** (Acetone-d_6): δ 7.00 (1H, ddd, ^3J = 7.3, ^4J = 4.9, ^5J = 0.8), 7.20 (1H, ddd, ^3J = 8.0, ^4J = 5.9, ^5J = 2.6), 7.29 (2H, m), 7.43 (1H, dd, ^3J = 8.1, ^4J = 1.4), 7.70 (1H, ddd, ^3J = 8.4, ^4J = 7.0, ^5J = 1.9), 7.85 (1H, d, ^3J = 8.4), 8.25 (1H, dd, ^3J = 5.1, ^4J = 1.5), 10.05 (1H, br s);

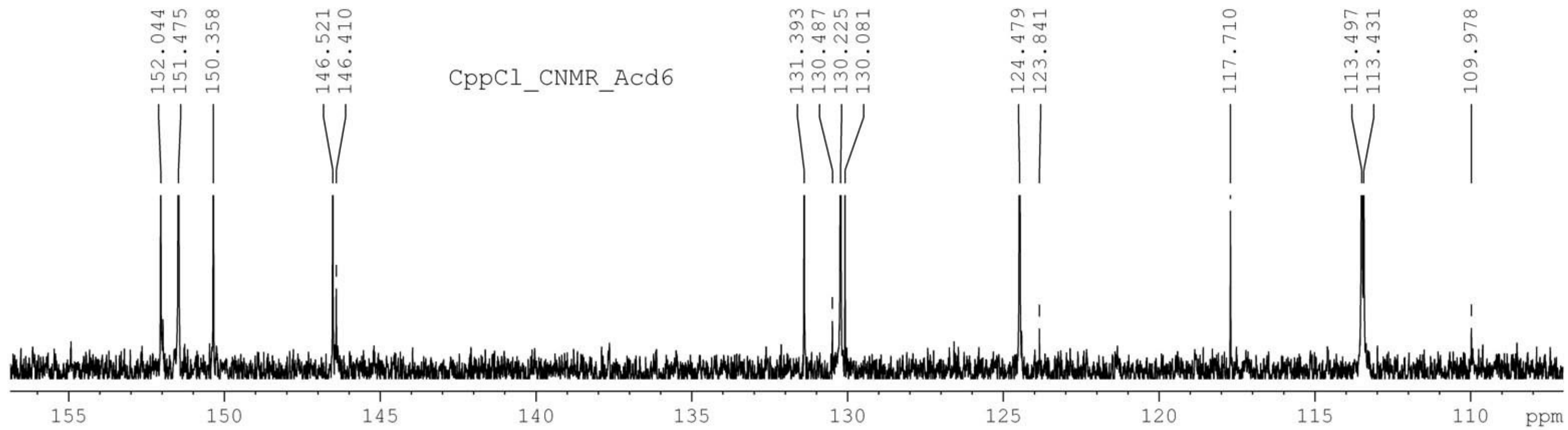


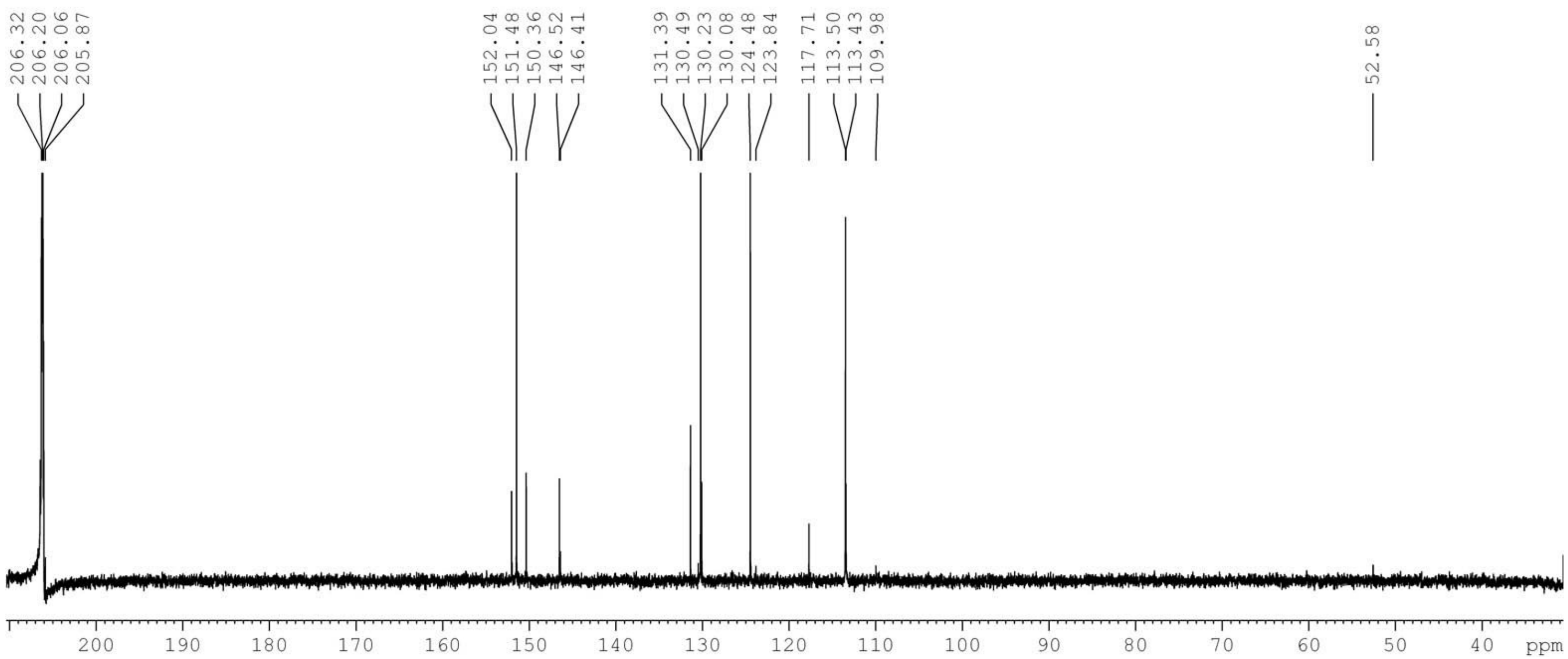
1.2.1.18. **CooCl** ($CDCl_3$) δ 7.08 (1H, ddd, ^3J = 7.6, ^4J = 5.1, ^5J = 0.9), 7.27 (1H, ddd, ^3J = 8.5, ^4J = 6.4, ^5J = 2.1; includes residual $CHCl_3$ solvent), 7.34 (2H, m), 7.52 (1H, dd, ^3J = 7.9, ^4J = 1.4), 7.78 (1H, ddd, ^3J = 8.9, ^4J = 7.2, ^5J = 1.9), 8.11 (1H, d, ^3J = 8.3), 8.48 (1H, d, ^3J = 5.1), 10.50 (1H, br s);



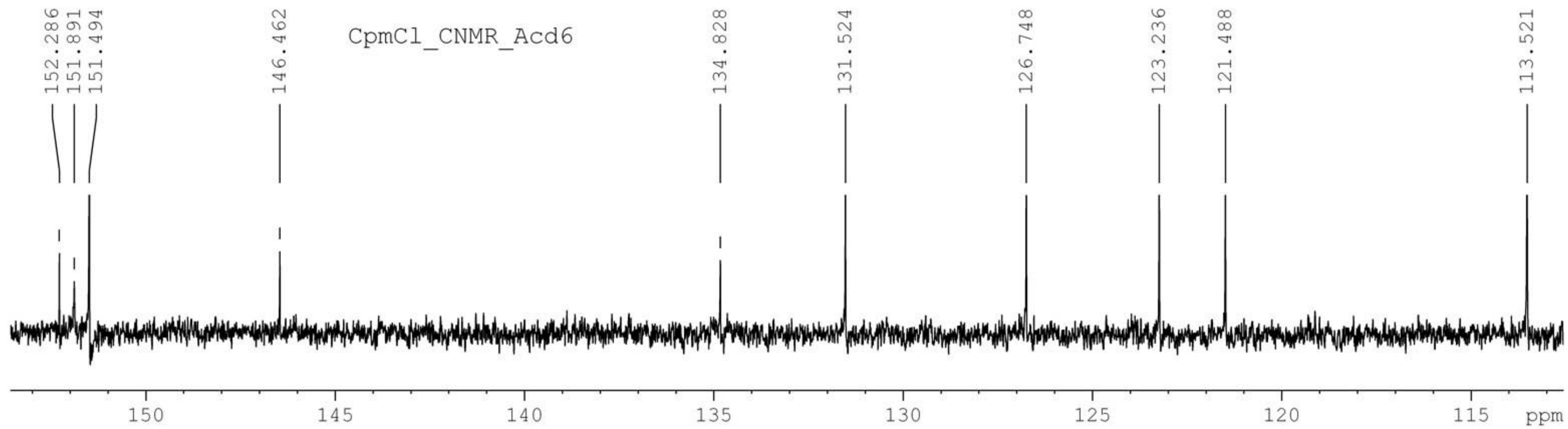
1.2.2. ^{13}C NMR data and spectra (400 MHz, Acetone-d_6)

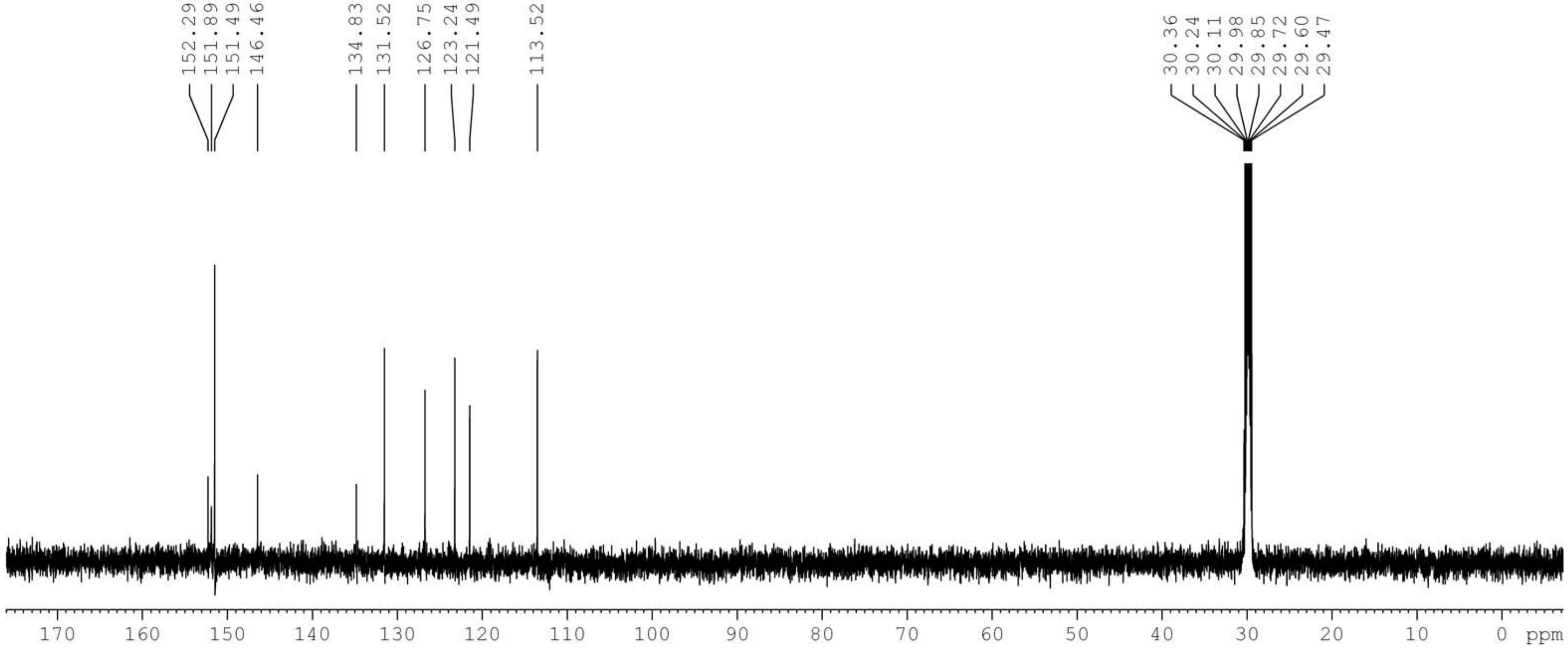
1.2.2.1. **CppCl**: δ 113.43/113.50, 124.48, 130.08/130.23, 131.39, 146.52, 150.36, 151.48, 152.05;



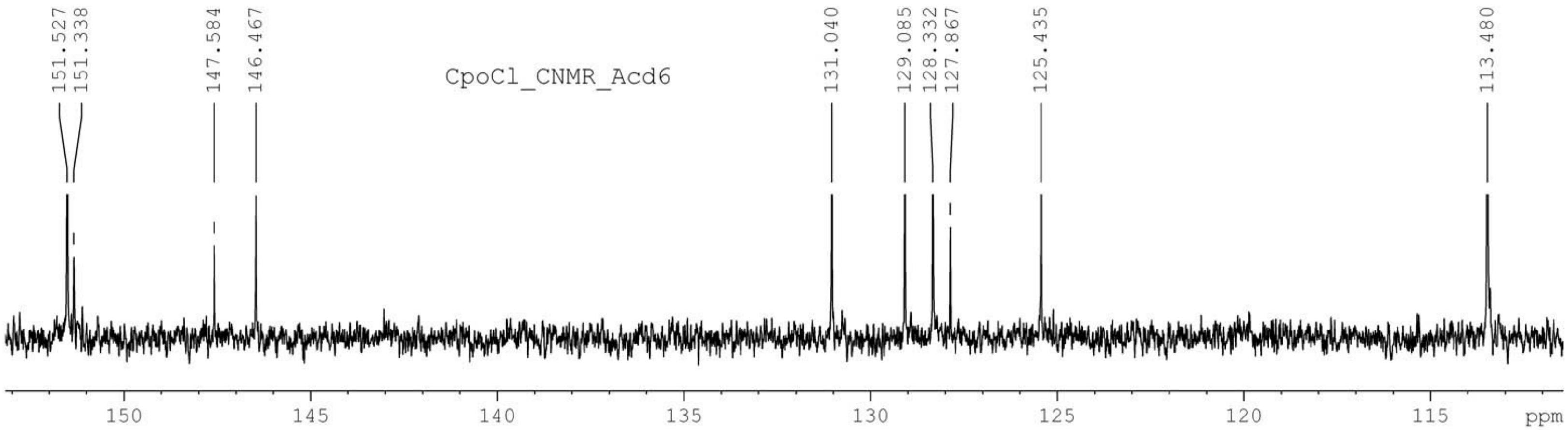


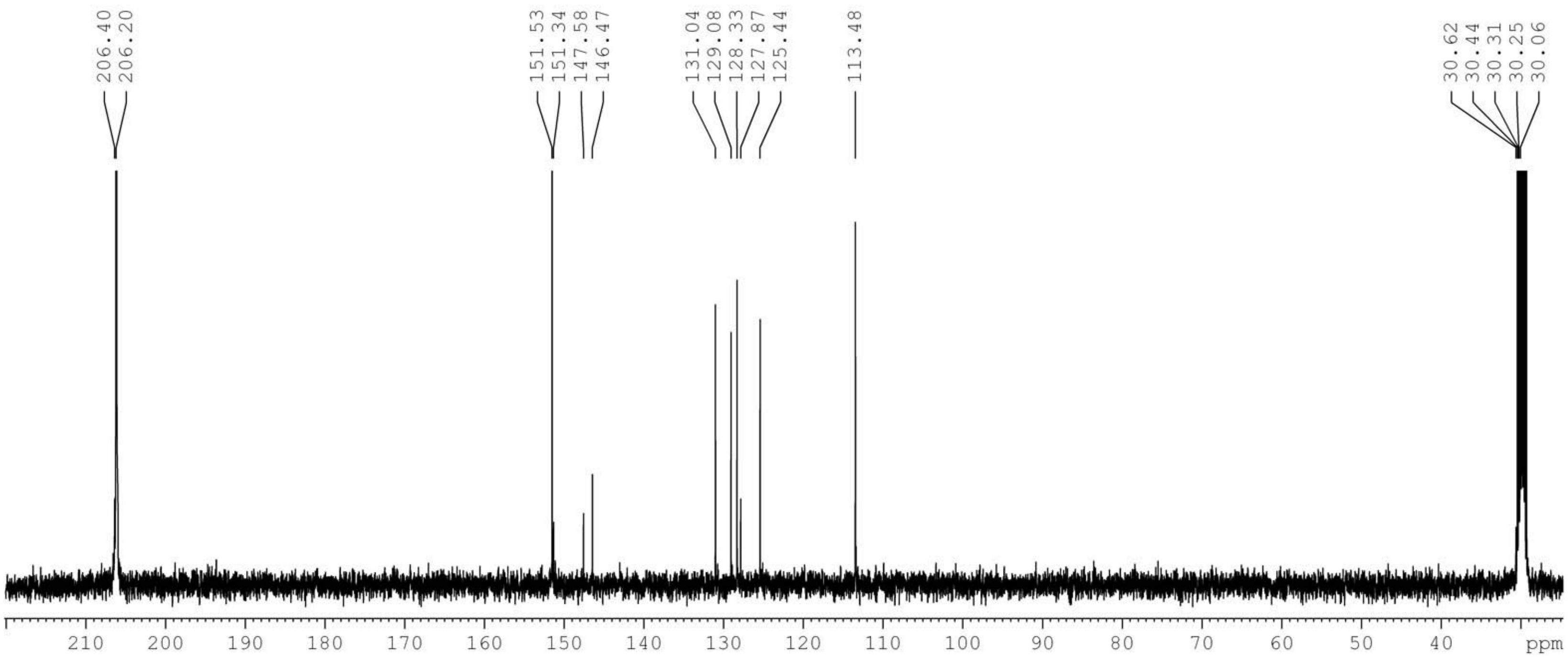
1.2.2.2. **CpmCl**: δ 113.52, 121.49, 123.24, 126.75, 131.52, 134.82, 146.46, 151.49, 151.89, 152.29;



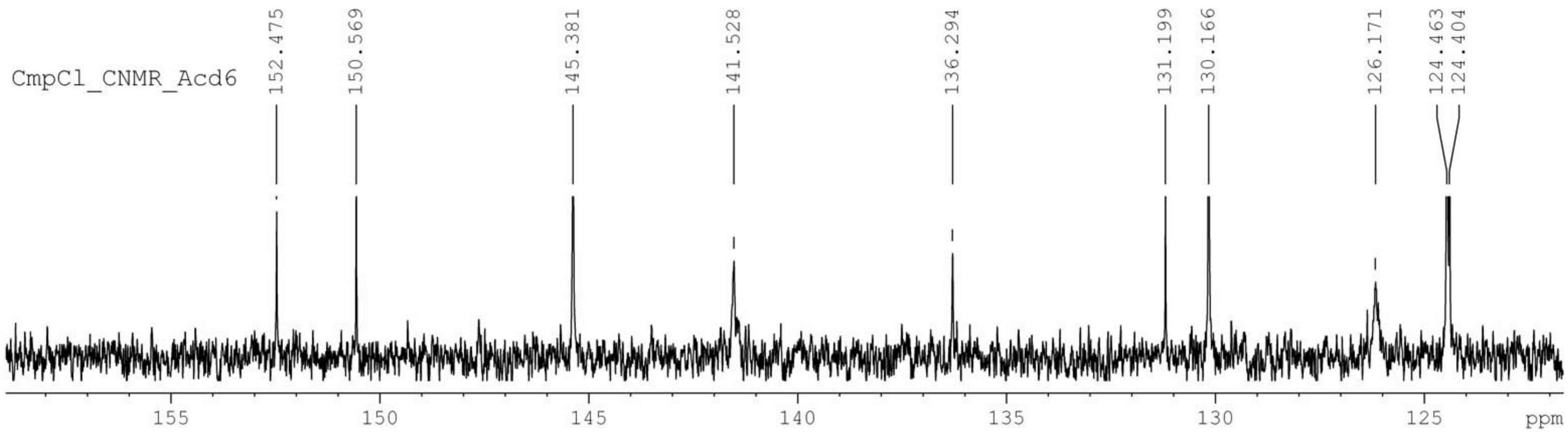


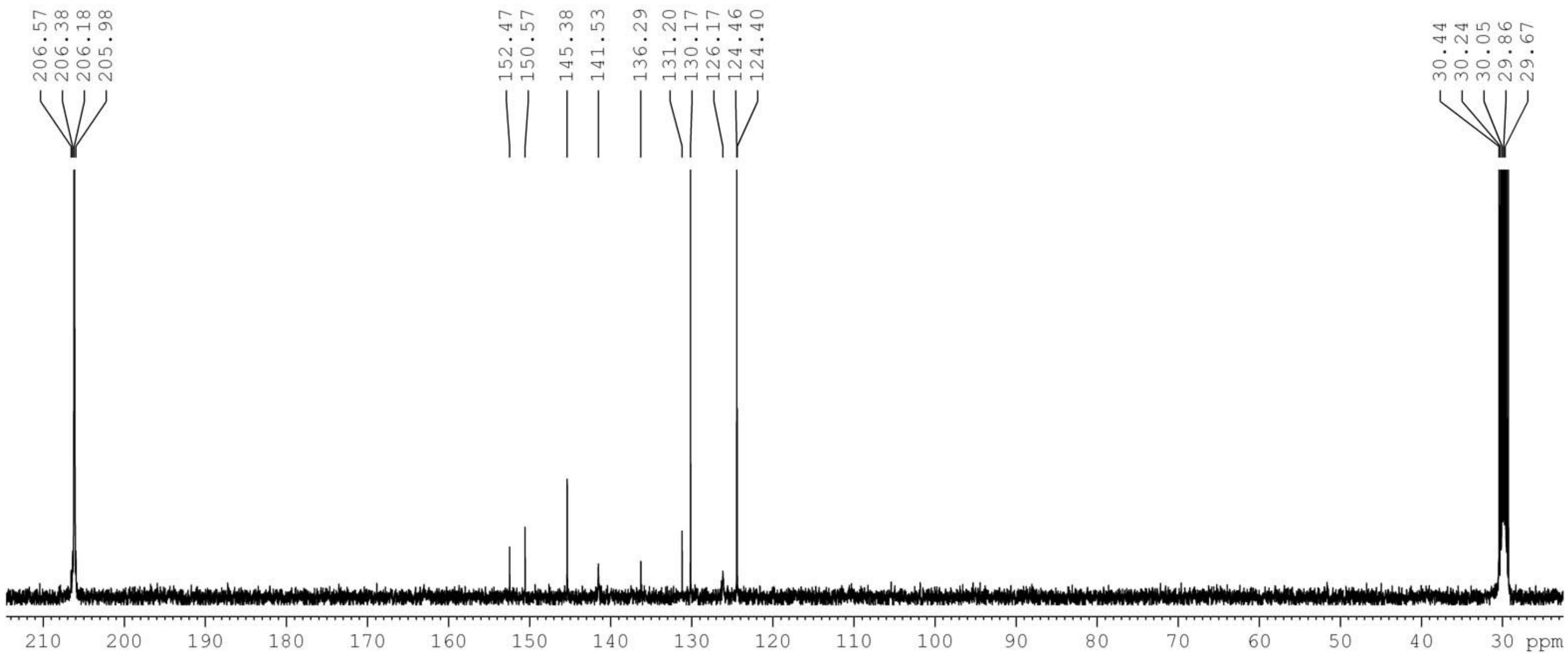
1.2.2.3. **CpoCl**: δ 113.48, 125.43, 127.87, 128.33, 129.08, 131.04, 146.47, 147.58, 151.34, 151.53;



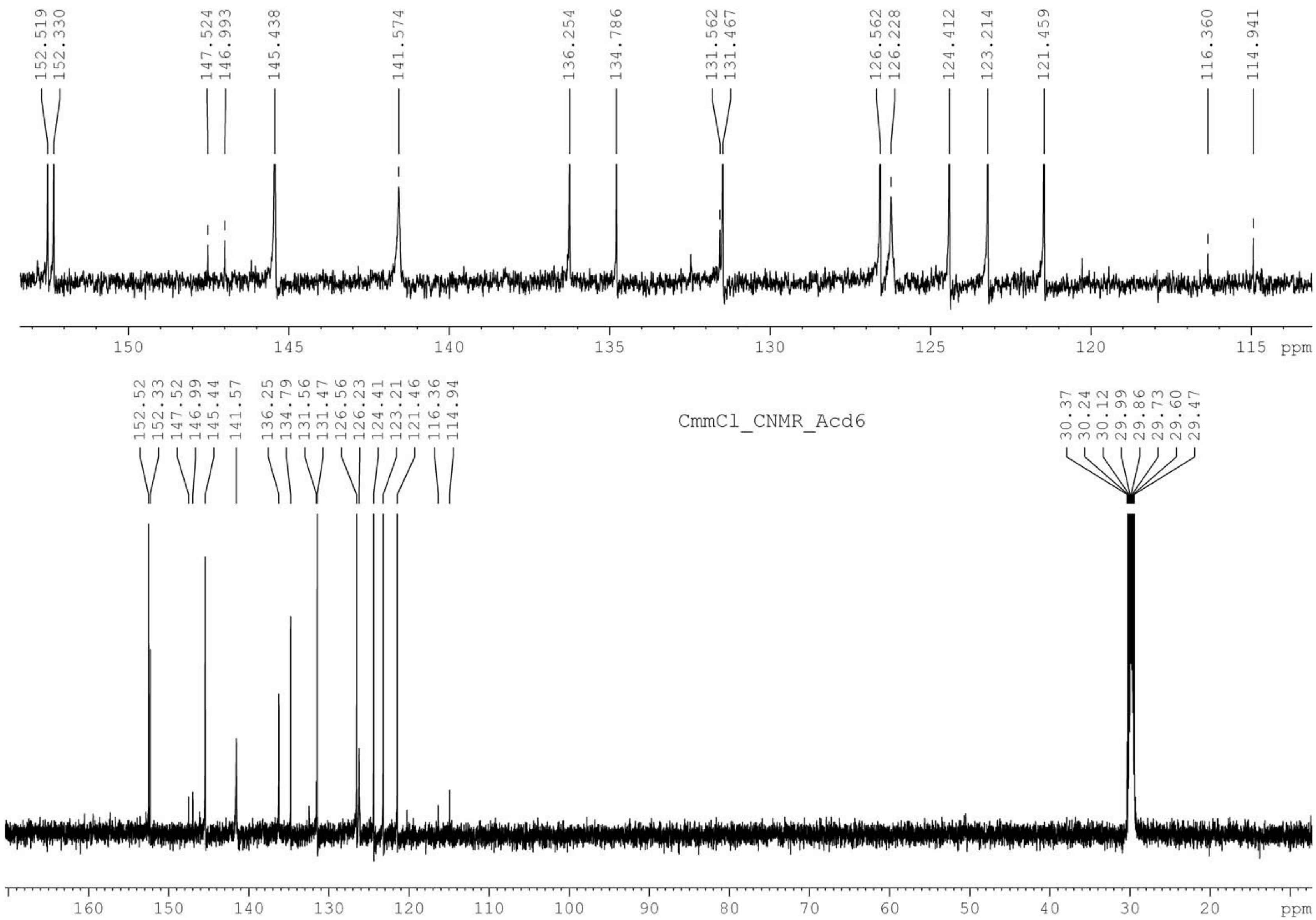


1.2.2.4. **CmpCl** δ 124.40, 124.46, 126.17, 130.16, 131.20, 136.29, 141.52, 145.38, 150.56, 152.47;

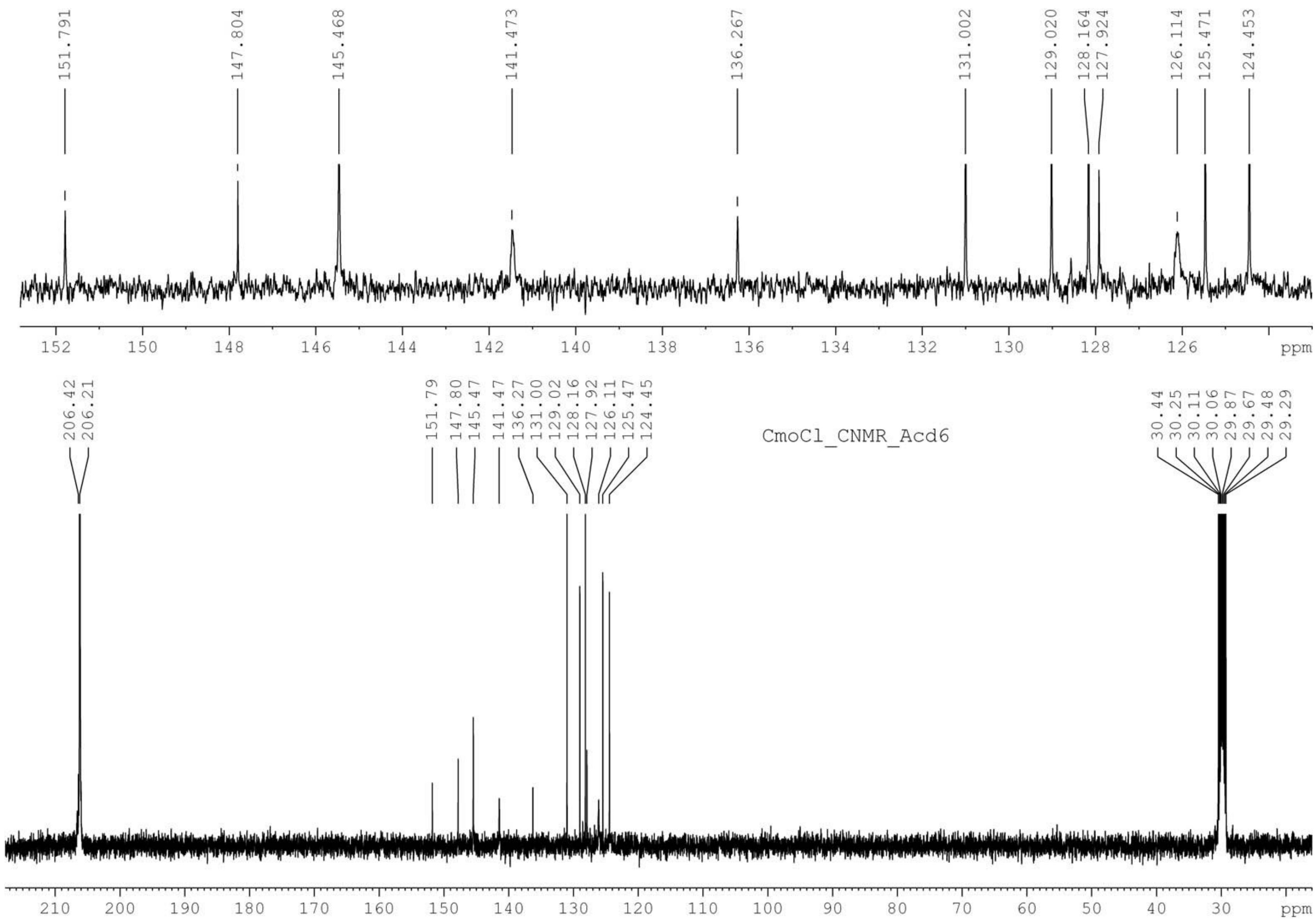




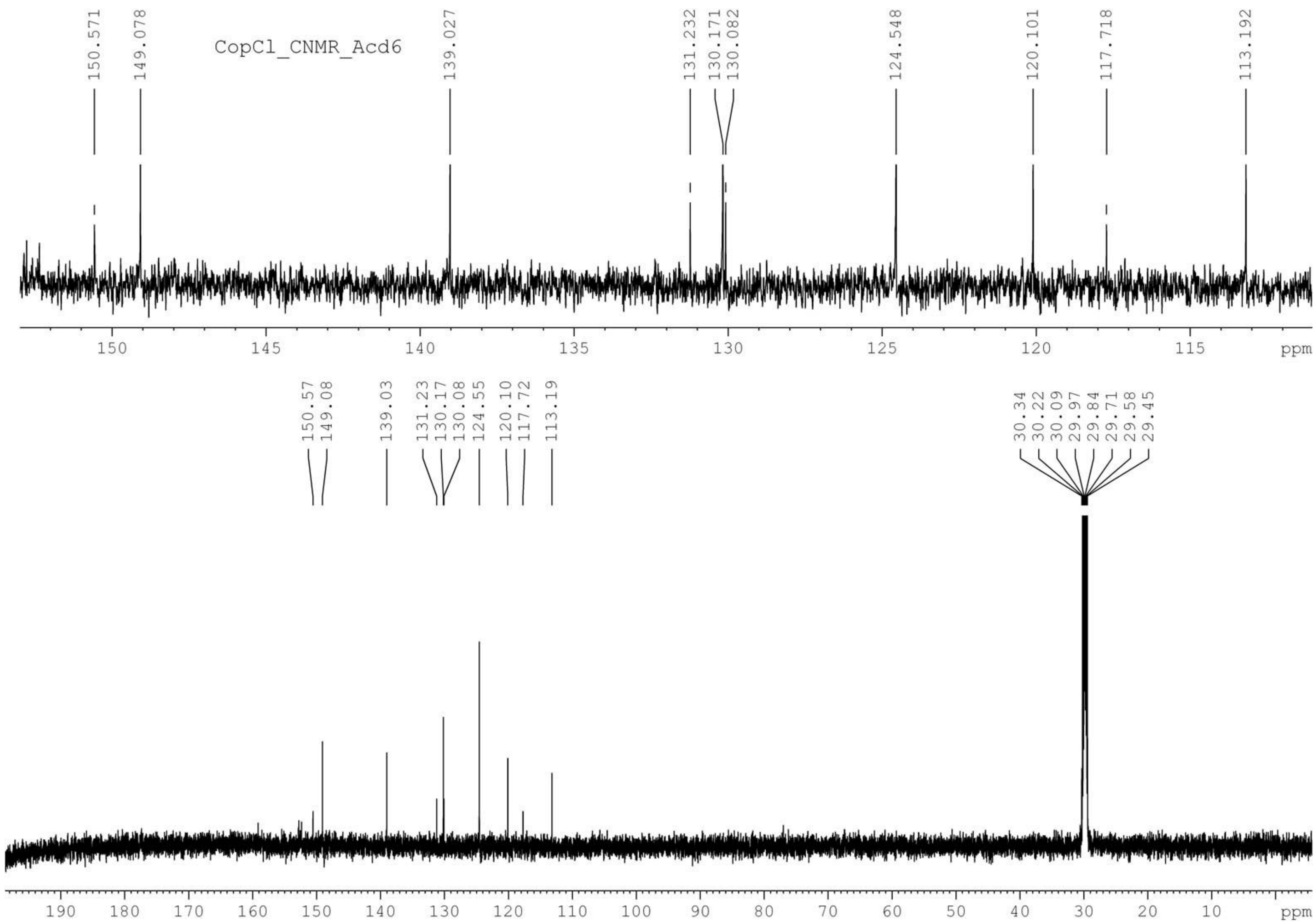
1.2.2.5. **CmmCl**: δ 121.46, 123.21, 124.41, 126.23, 126.56, 131.47/131.56, 134.79, 136.25, 141.57, 145.44, 152.33, 152.52;



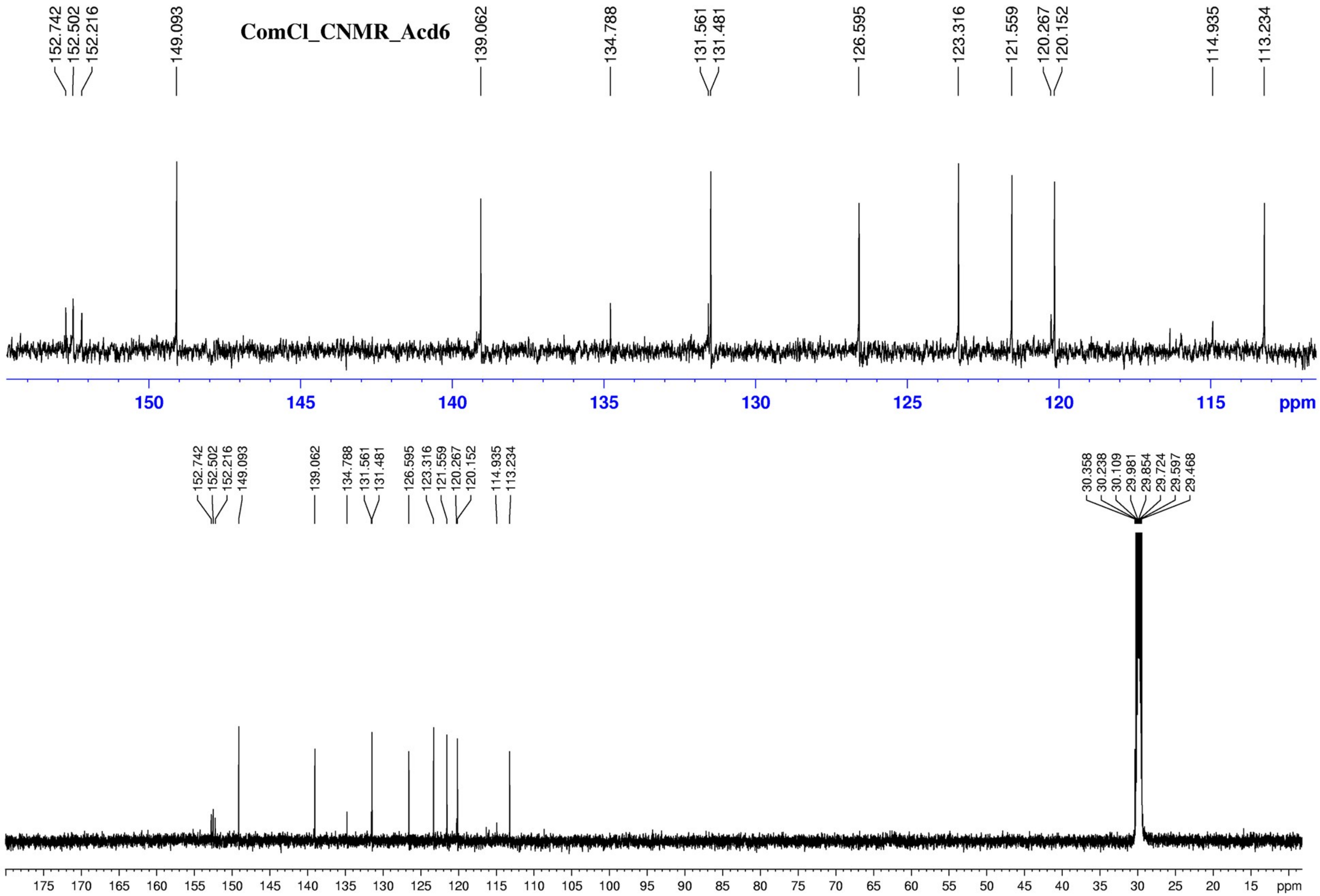
1.2.2.6. **CmoCl**: δ 124.45, 125.47, 126.11, 127.92, 128.16, 129.02, 131.00, 136.27, 141.47, 145.47, 147.80, 151.79;



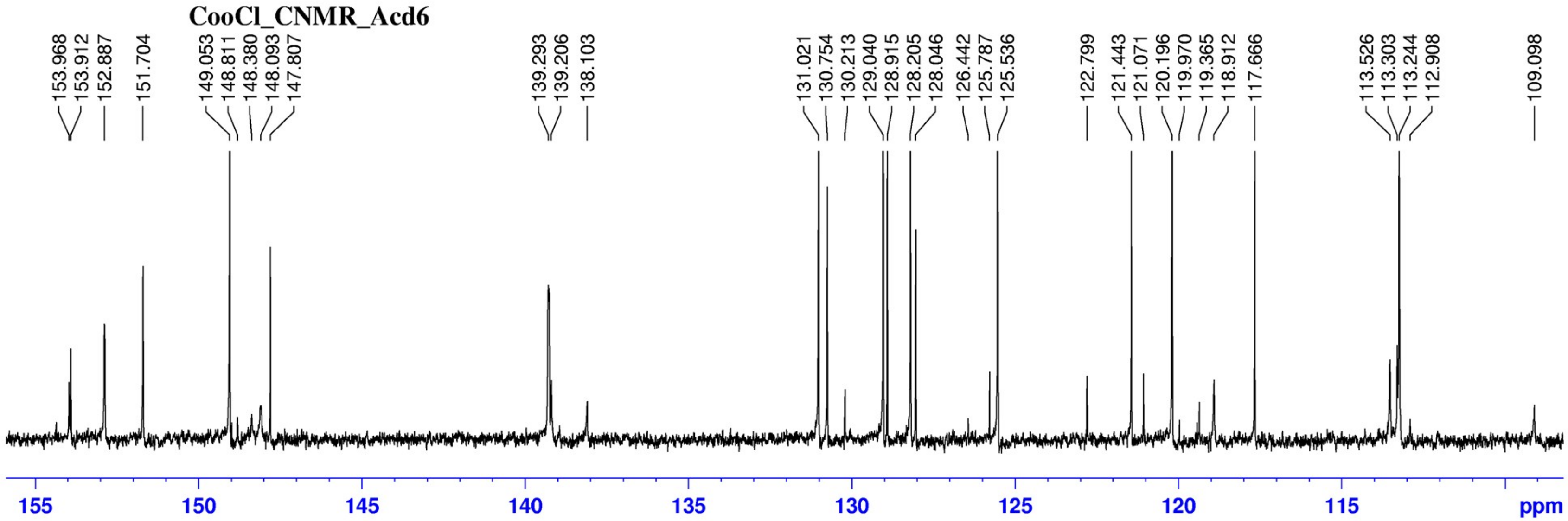
1.2.2.7. **CopCl**: δ 113.22, 117.73, 120.13, 124.54, 130.17, 139.02, 149.08, 150.59, 152.36, 152.78.

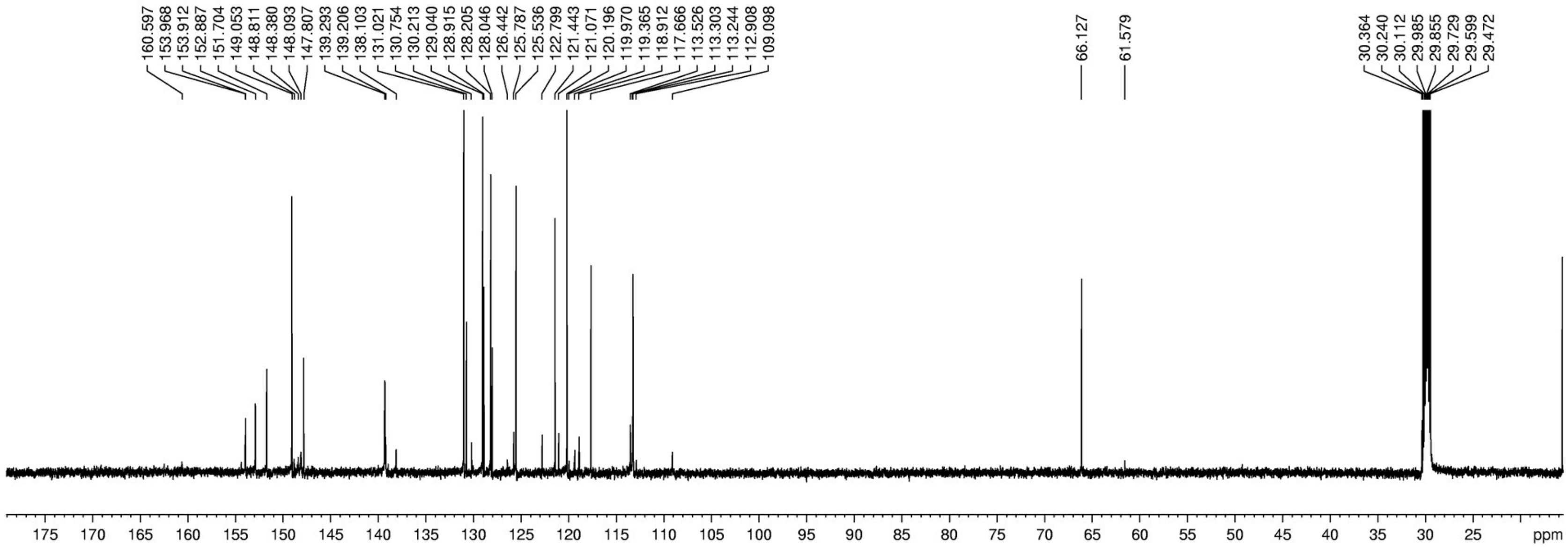


1.2.2.8. **ComCl**: δ 113.23, 120.15, 121.56. 123.32, 126.59, 131.48/131.56, 134.79, 139.06, 149.09, 152.22, 152.50, 152.74;



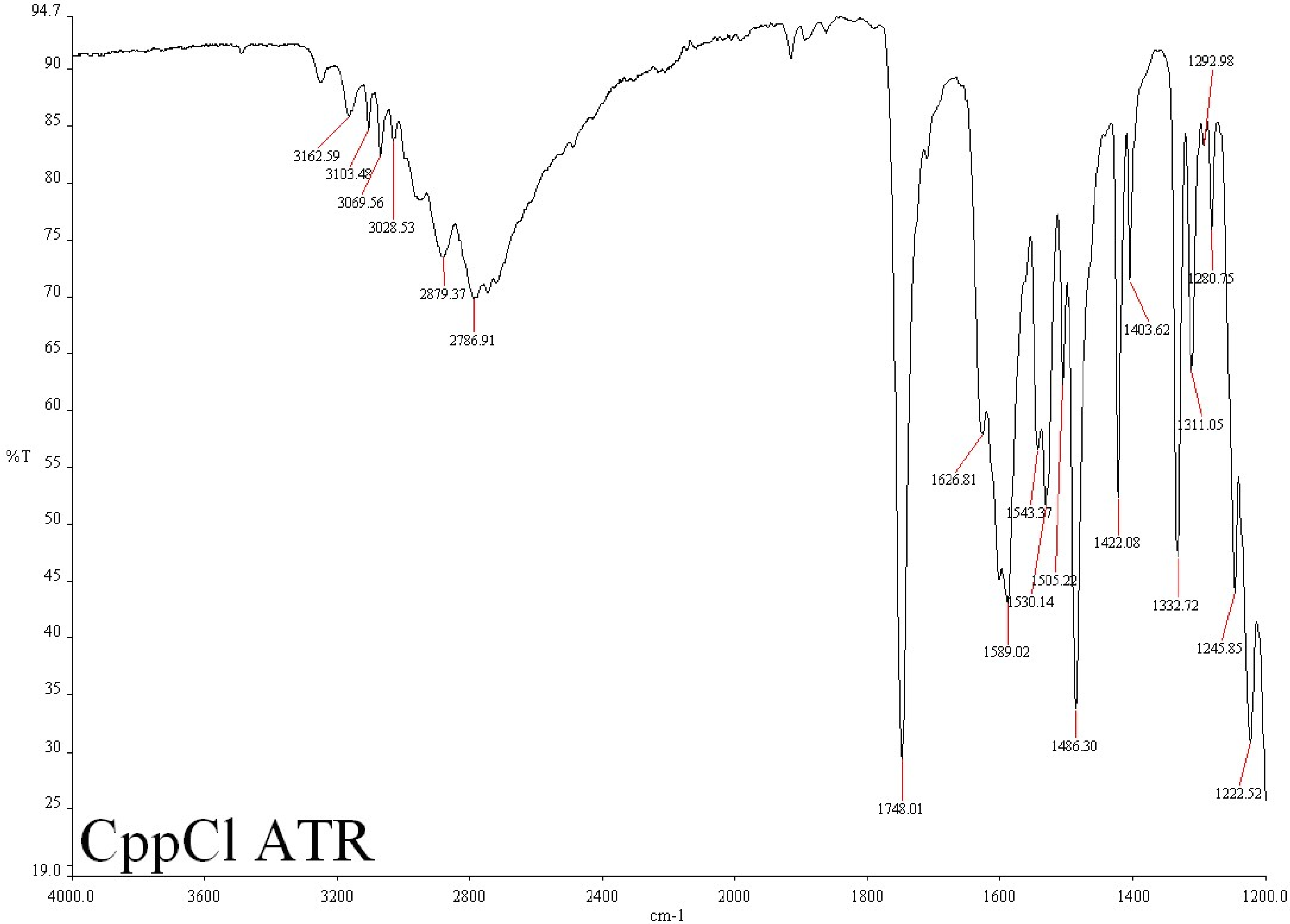
1.2.2.9. **CooCl**: δ 113.24, 120.20, 125.54, 128.05, 128.20, 129.04, 131.02, 139.29, 147.81, 149.05, 151.70, 152.88;



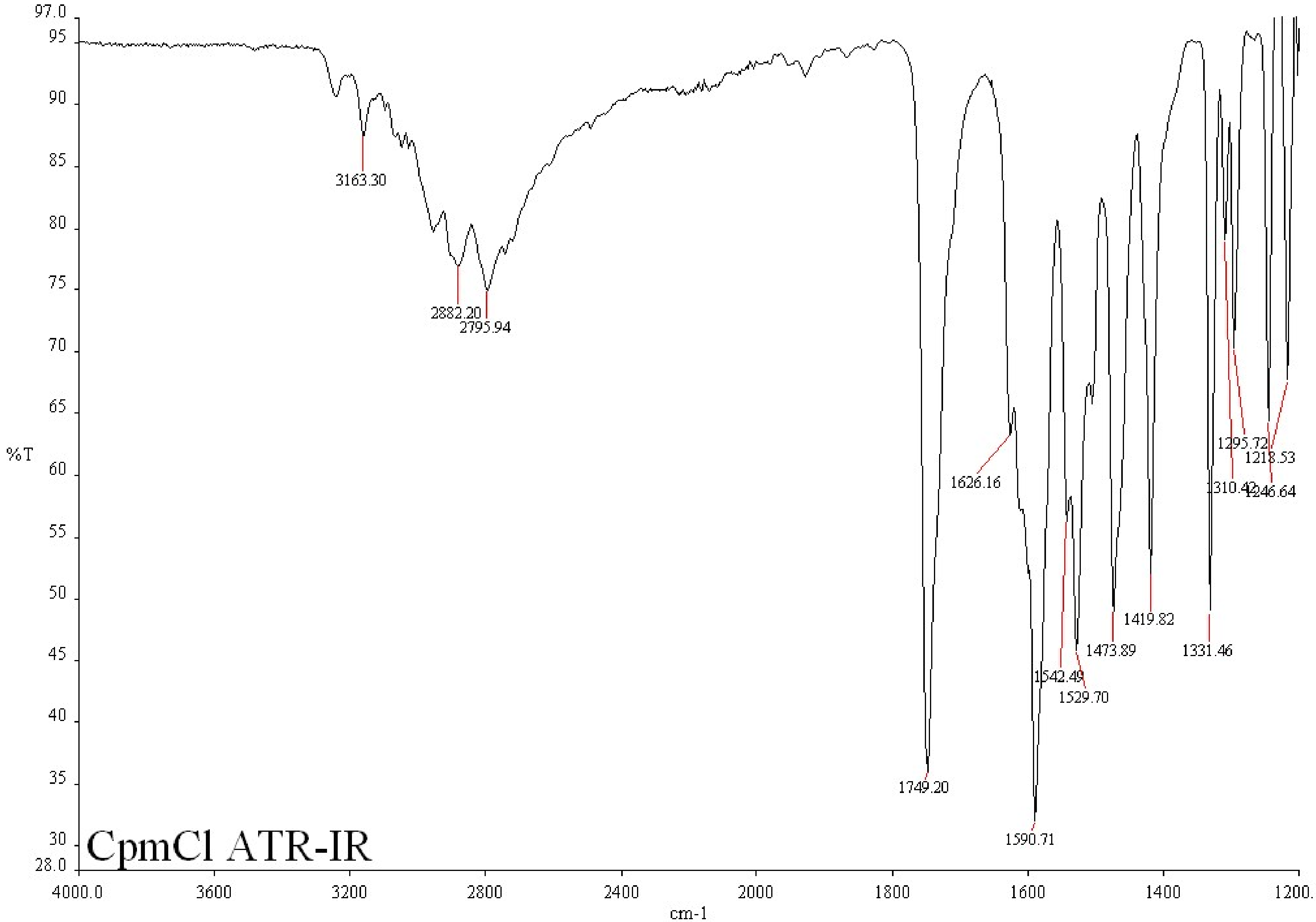


1.2.3. **<u>IR (ATR) data and spectra</u>**

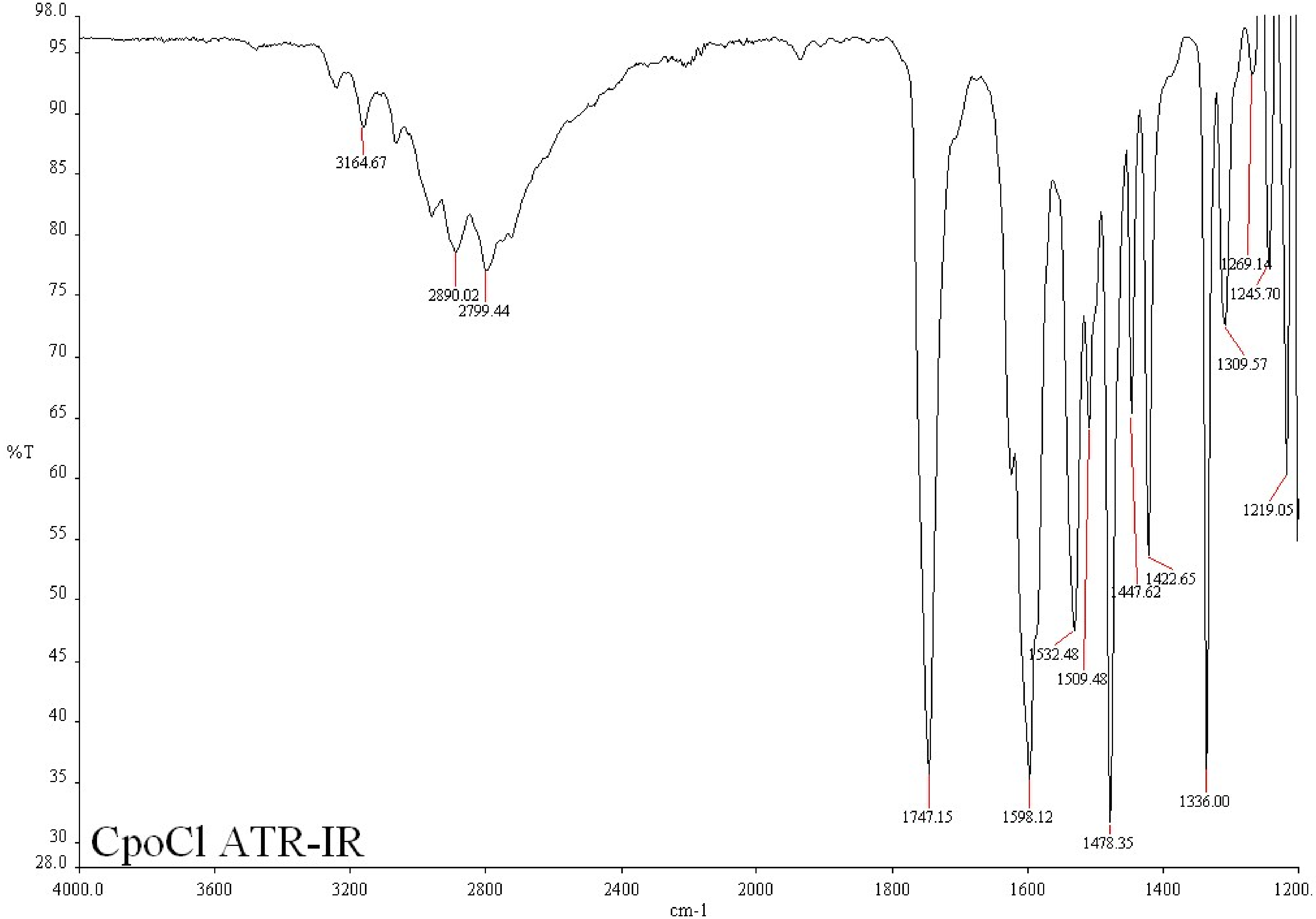
1.2.3.1. **CppCl**: 3163 (w), 3103 (w), 3070 (w), 3029 (w), 2879 (w), 2787 (w), 1748 (s), 1627 (m), 1589 (s), 1543 (m), 1530 (m), 1505 (w), 1486 (s), 1422 (m).



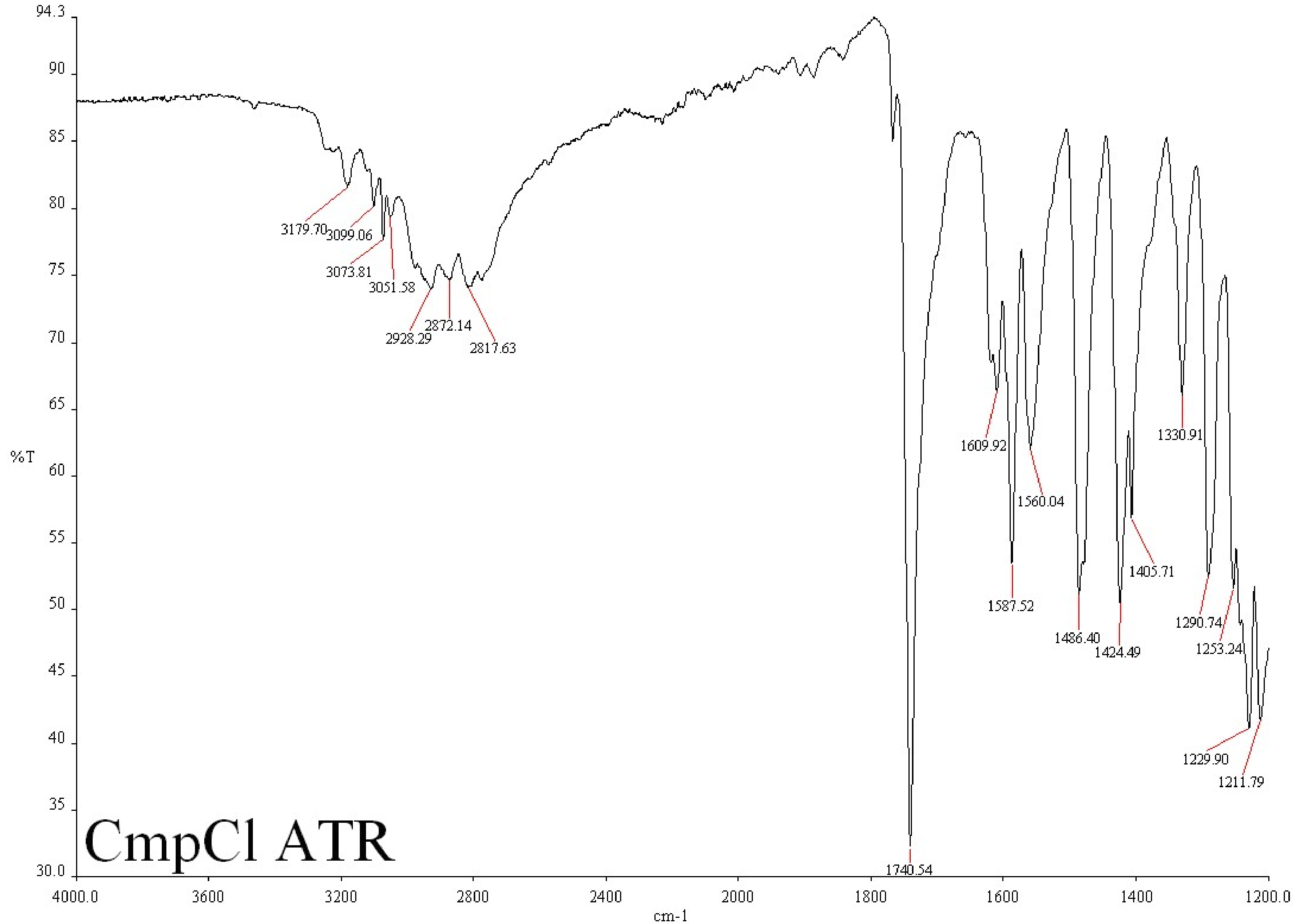
1.2.3.2. **CpmCl**: 3163 (w), 2882 (m), 2796 (m), 1749 (s), 1626 (m), 1591 (s), 1542 (s), 1530 (s), 1474 (s), 1420 (s).



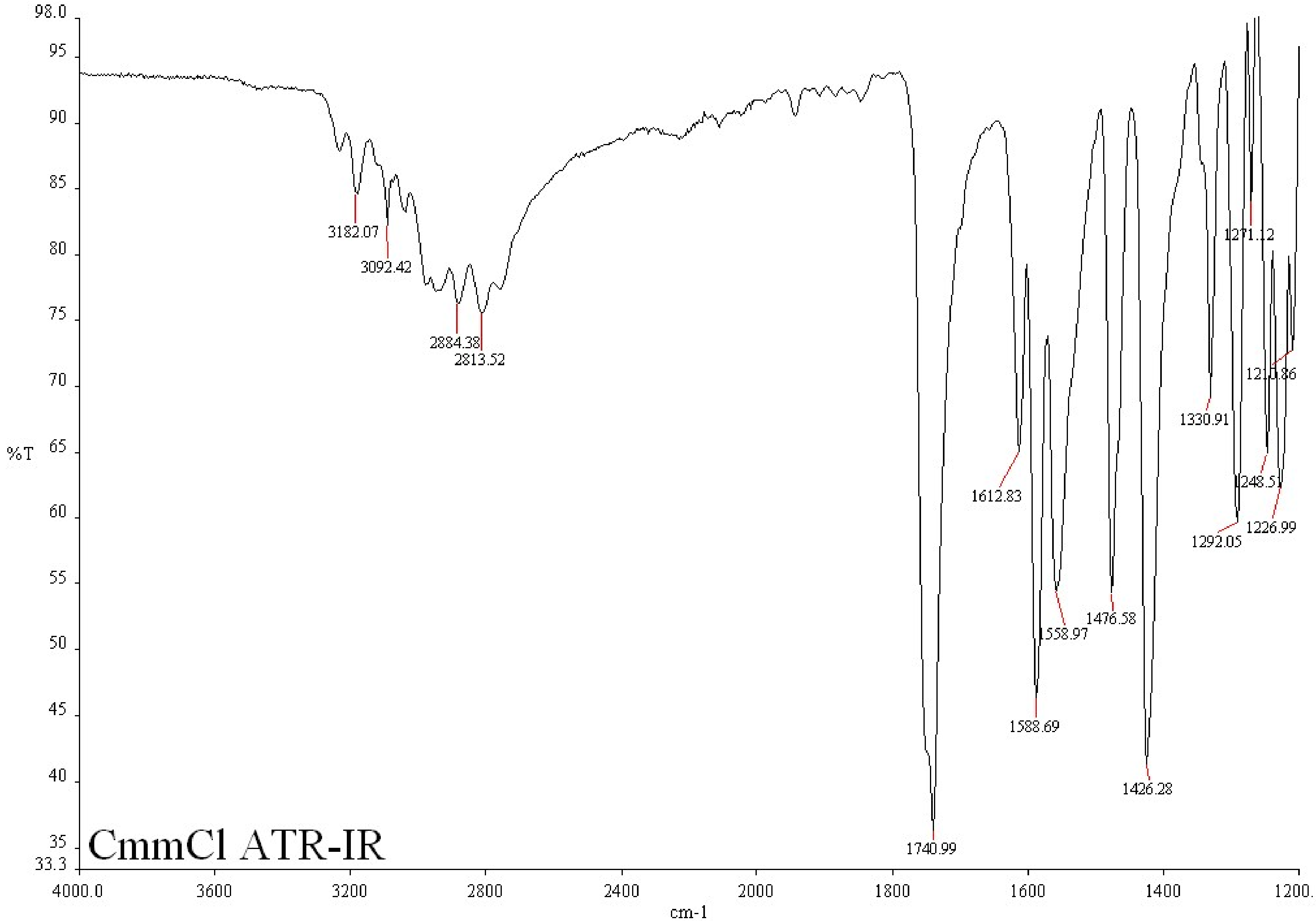
1.2.3.3. **CpoCl**: 3165 (w), 2890 (m), 2799 (m), 1747 (s), 1598 (s), 1532 (s), 1509 (m), 1478 (s), 1448 (m), 1423 (s).



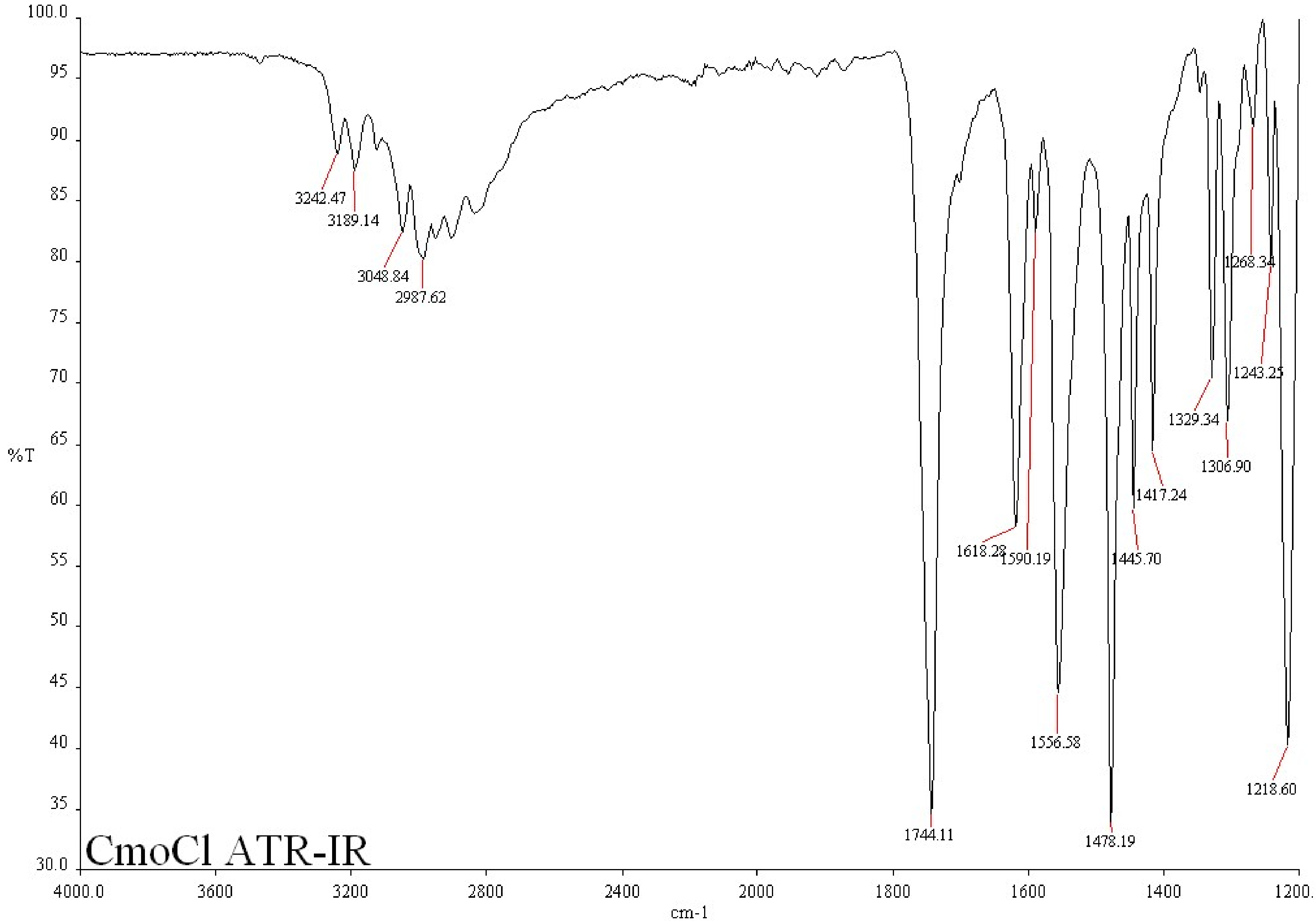
1.2.3.4. **CmpCl**: 3180 (w), 3099 (w), 3074 (w), 3052 (w), 2928 (w), 2872 (w), 2818 (w), 1740 (s), 1610 (m), 1587 (s), 1560 (m), 1486 (s), 1424 (s), 1406 (m).



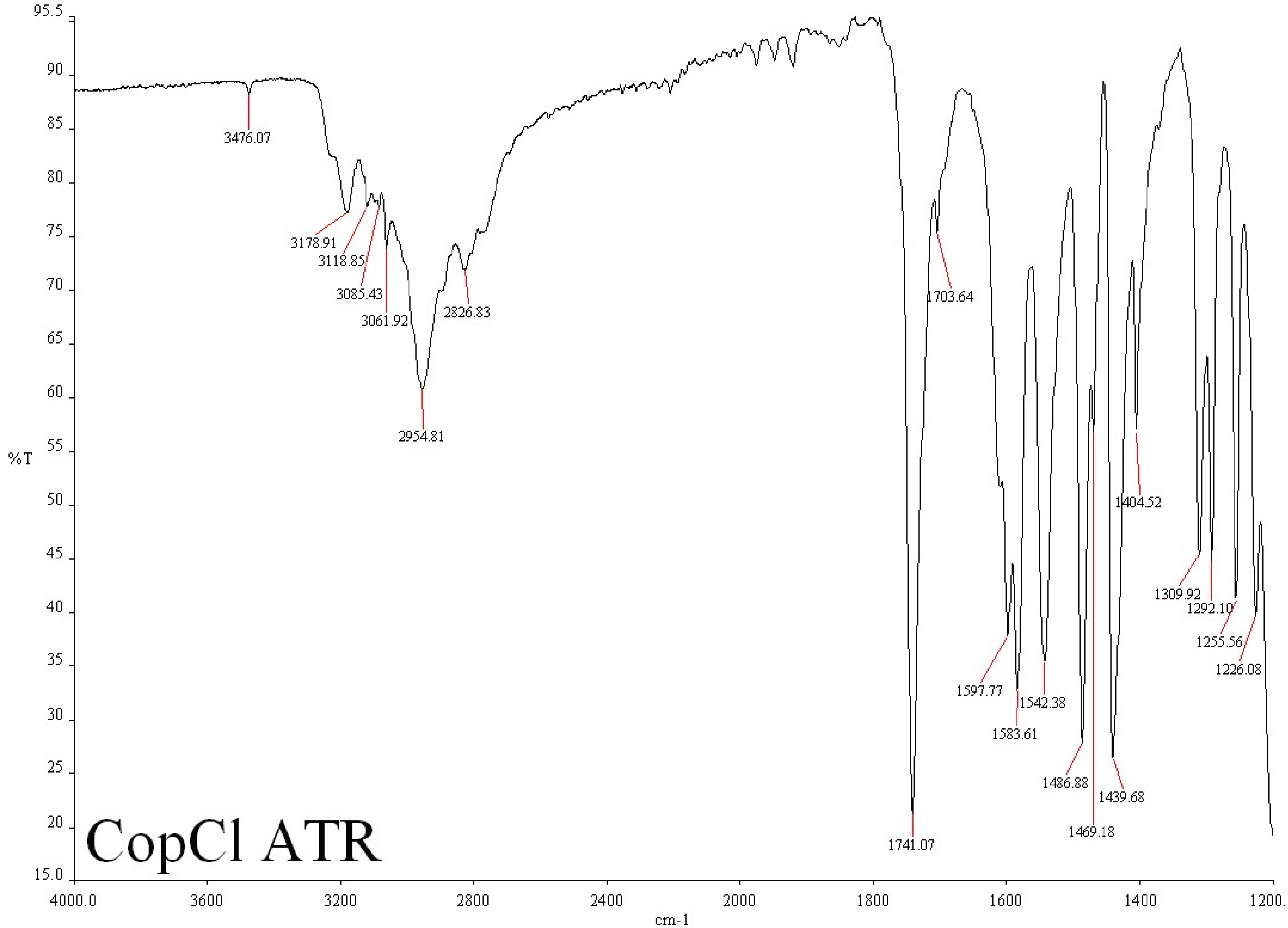
1.2.3.5. **CmmCl**: 3182 (w), 3092 (w), 2884 (m), 2813 (m), 1741 (s), 1613 (m), 1589 (s), 1559 ()s), 1477 (s), 1426 (s).



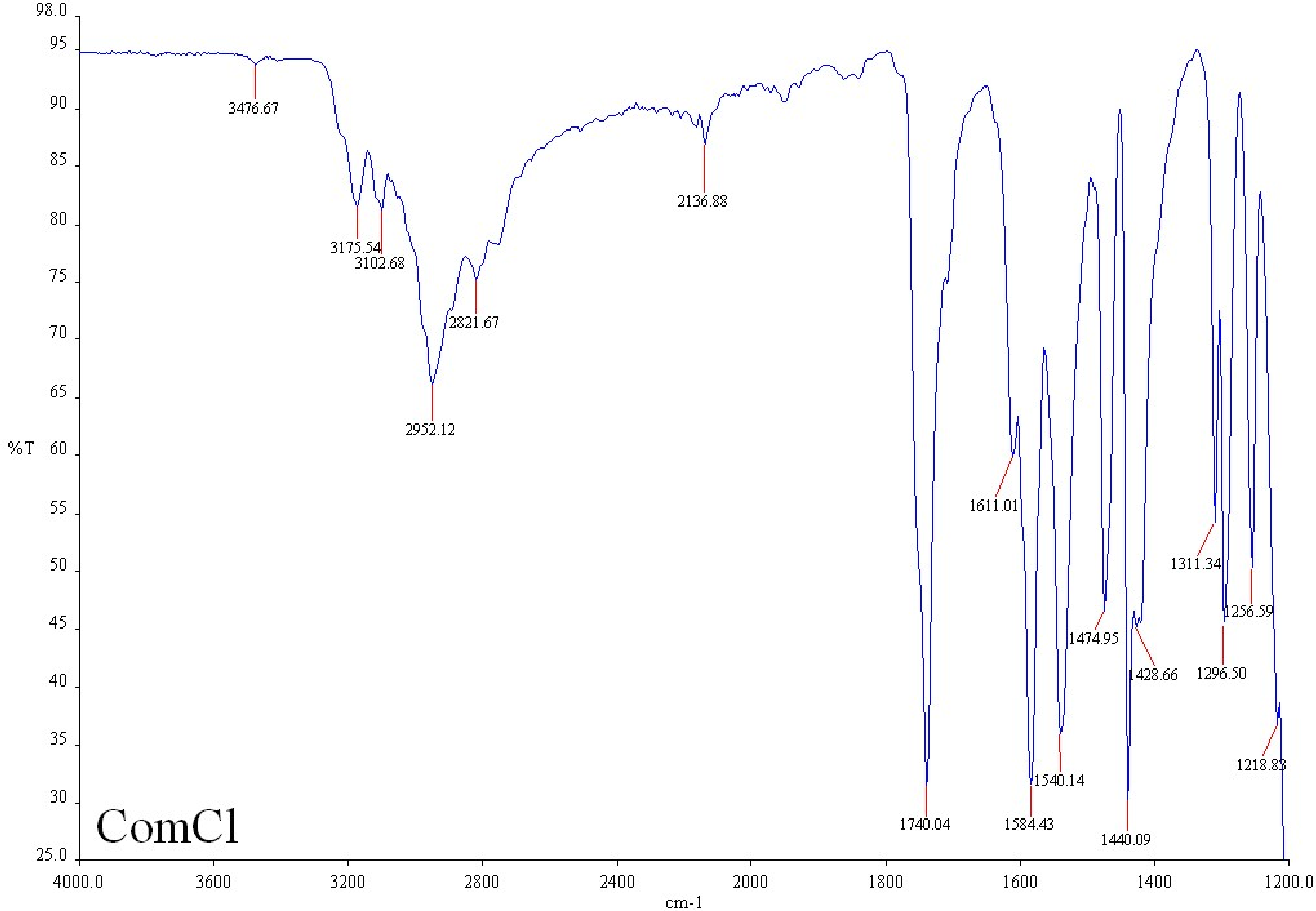
1.2.3.6. **CmoCl**: 3242 (w), 3189 (w), 3049 (w), 2988 (m), 1744 (s), 1618 (m), 1590 (w), 1557 (s), 1478 (s), 1446 (m), 1417 (m).



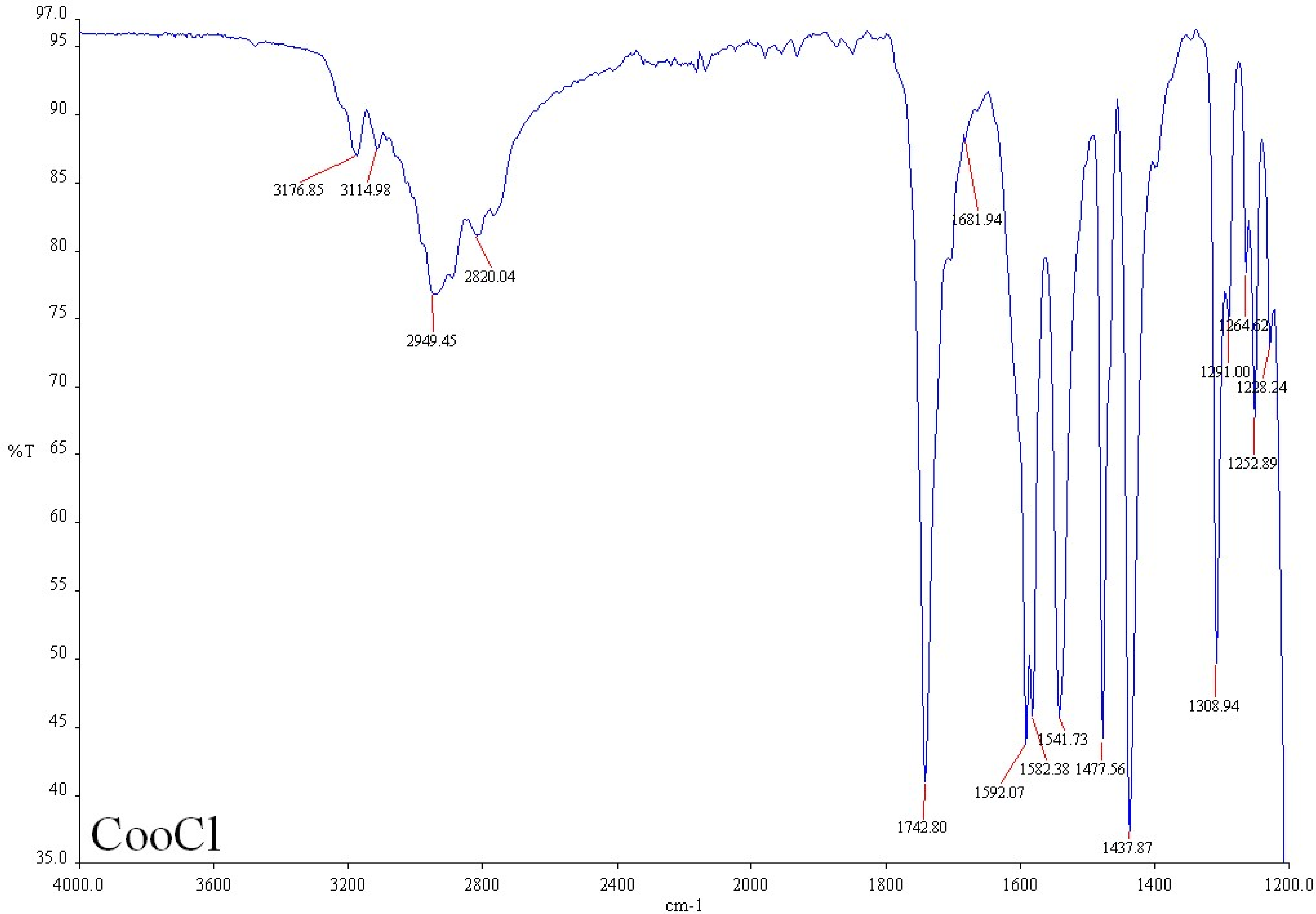
1.2.3.7. **CopCl**: 3179 (w), 3119 (w), 3084 (w), 3062 (w), 2955 (m), 2827 (w), 1741 (s), 1704 (w), 1598 (s), 1584 (s), 1542 (s), 1487 (s), 1440 (s), 1404 (m).



1.2.3.8. **ComCl**: 3477 (w), 3176 (w), 3103 (w), 2952 (m), 2822 (m), 2137 (w), 1740 (s), 1611 (m), 1584 (s), 1540 (s), 1475 (s), 1440 (s), 1429 (s).



1.2.3.9. **CooCl**: 3176 (w), 3115 (w), 2949 (m), 2820 (m), 1743 (s), 1682 (w), 1592 (s), 1582 (s), 1542 (s), 1478 (s), 1438 (s).



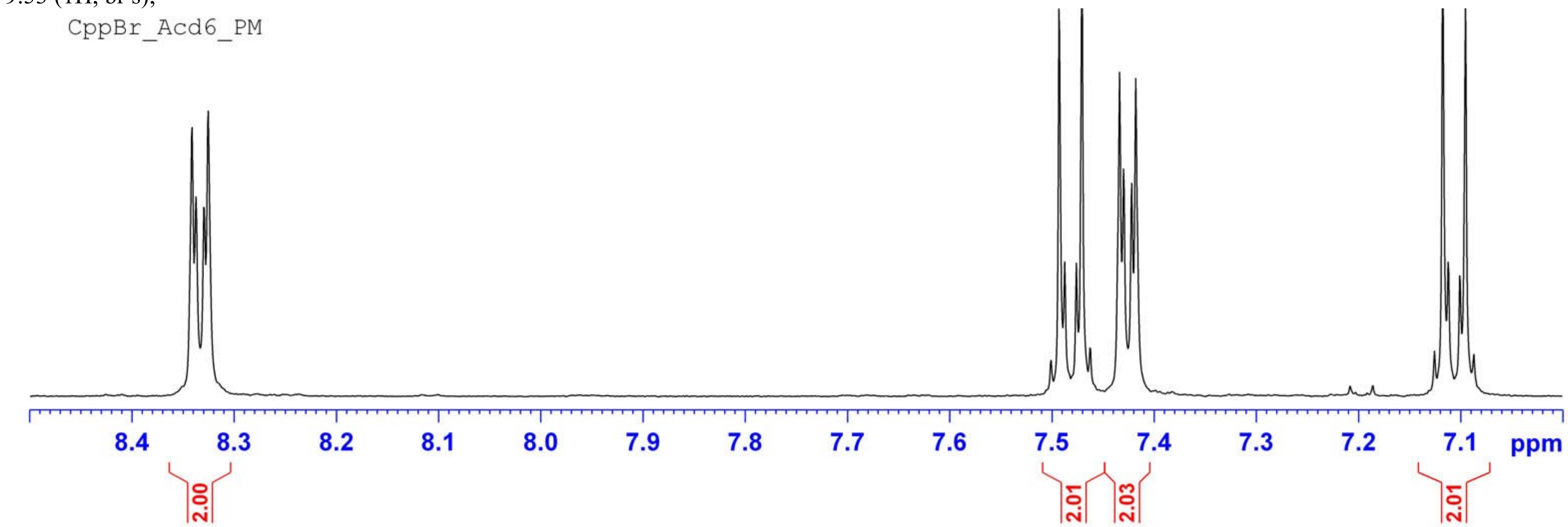
<u>1.3.</u> **CxxBr isomer grid**

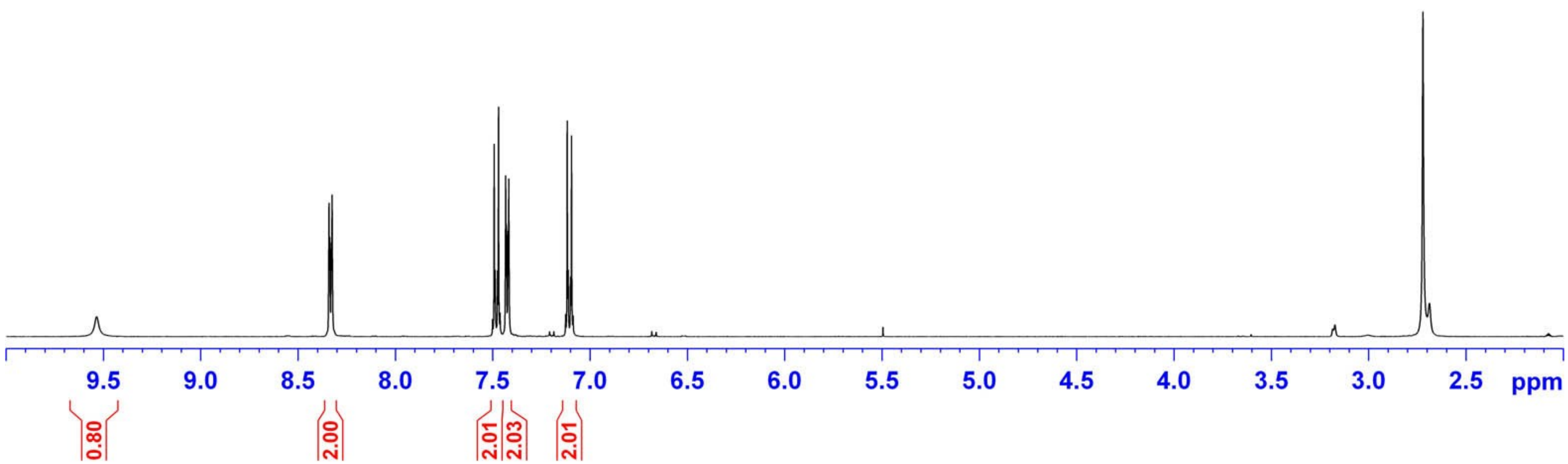
^{1}H NMR data	**pages 76-91**	(run in CD_3COCD_3, acetone-d_6 and $CDCl_3$)
^{13}C NMR data	**pages 92-99**	
Infra-red	**pages 100-107**	

Ab Initio calculations pages 108-116

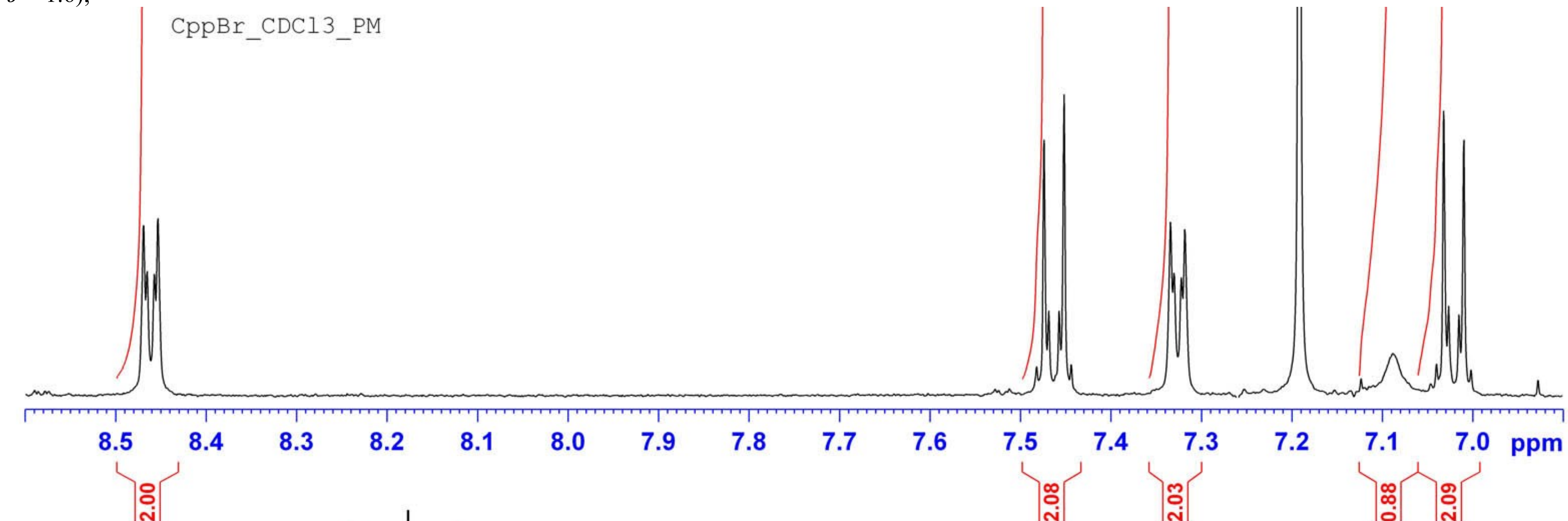
1.3.1. ^{1}H NMR data and spectra (400 MHz)

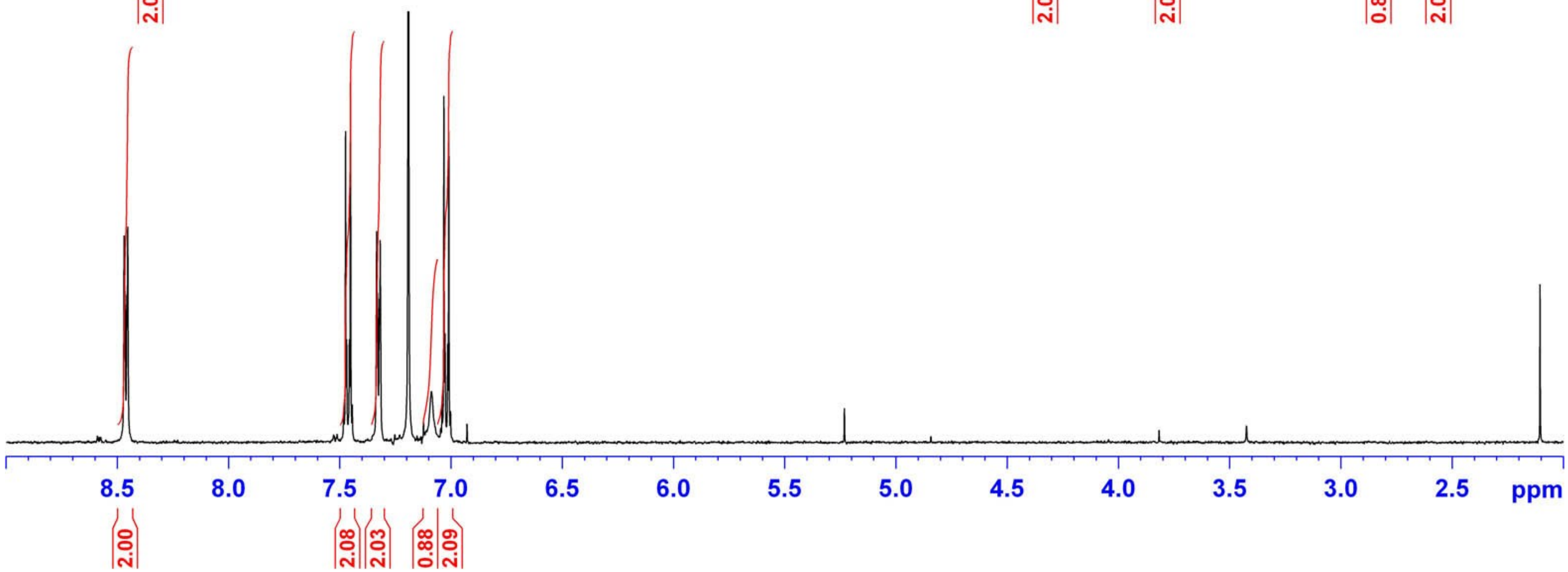
1.3.1.1. **CppBr** (Acetone-d6): δ 7.11 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.7), 7.42 (2H, dd, ^{3}J = 4.8, ^{4}J = 1.6), 7.48 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.7), 8.33 (2H, dd, ^{3}J = 4.8, ^{4}J = 1.6), 9.53 (1H, br s);



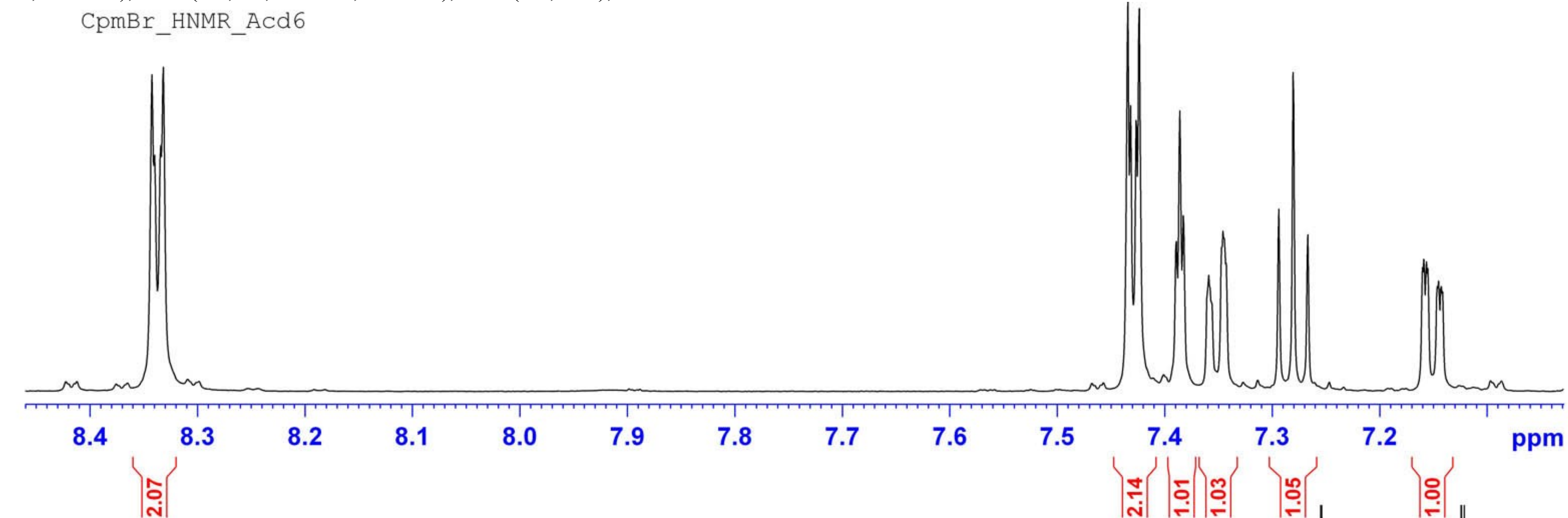


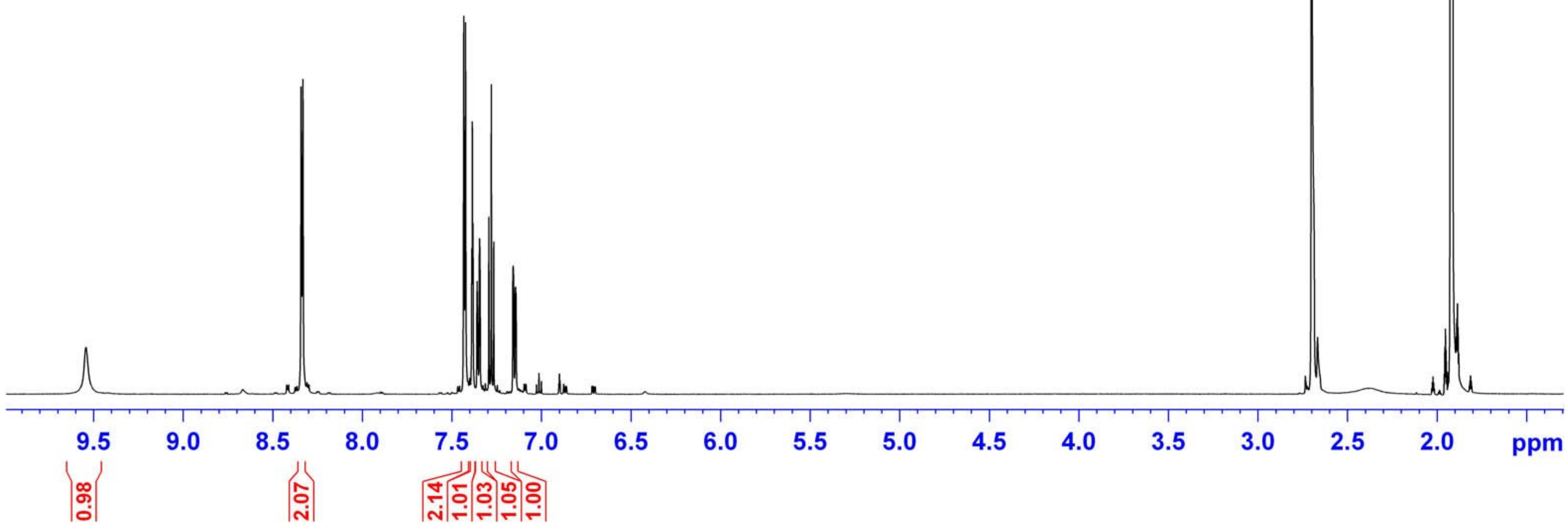
1.3.1.2. **CppBr** ($CDCl_3$) δ 7.02 (2H, dt, $^{3}J = 8.8$, $^{4}J = 2.5$), 7.09 (1H, br s), 7.33 (2H, dd, $^{3}J = 5$, $^{4}J = 1.6$), 7.46 (2H, dt, $^{3}J = 8.9$, $^{4}J = 2.7$), 8.46 (2H, dd, $^{3}J = 5.1$, $^{4}J = 1.6$);



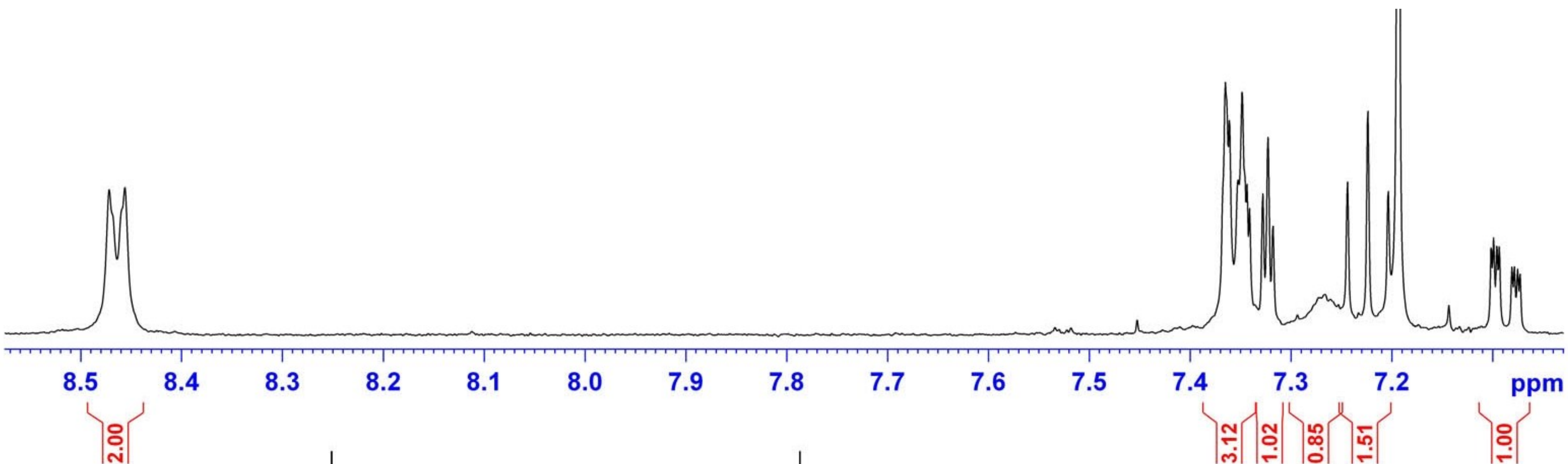


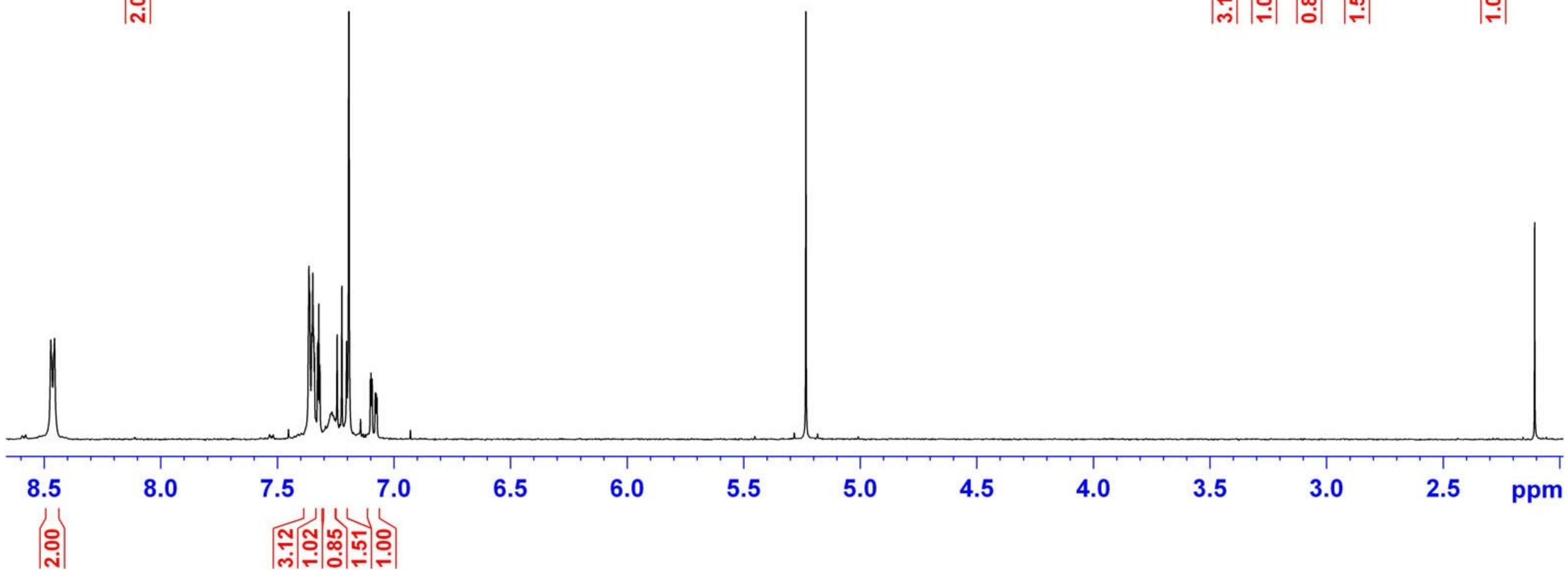
1.3.1.3. **CpmBr** (Acetone-d_6): δ 7.15 (1H, ddd, ^3J = 8.3, ^4J = 2.0, ^5J = 0.6), 7.28 (1H, t, ^3J = 8.1), 7.35 (1H, d, ^3J = 8.0), 7.39 (1H, t, ^3J =2.1), 7.43 (2H, dd, ^3J = 5.0, ^4J = 1.6), 8.34 (2H, dd, ^3J = 4.7, ^4J = 1.5), 9.54 (1H, br s);



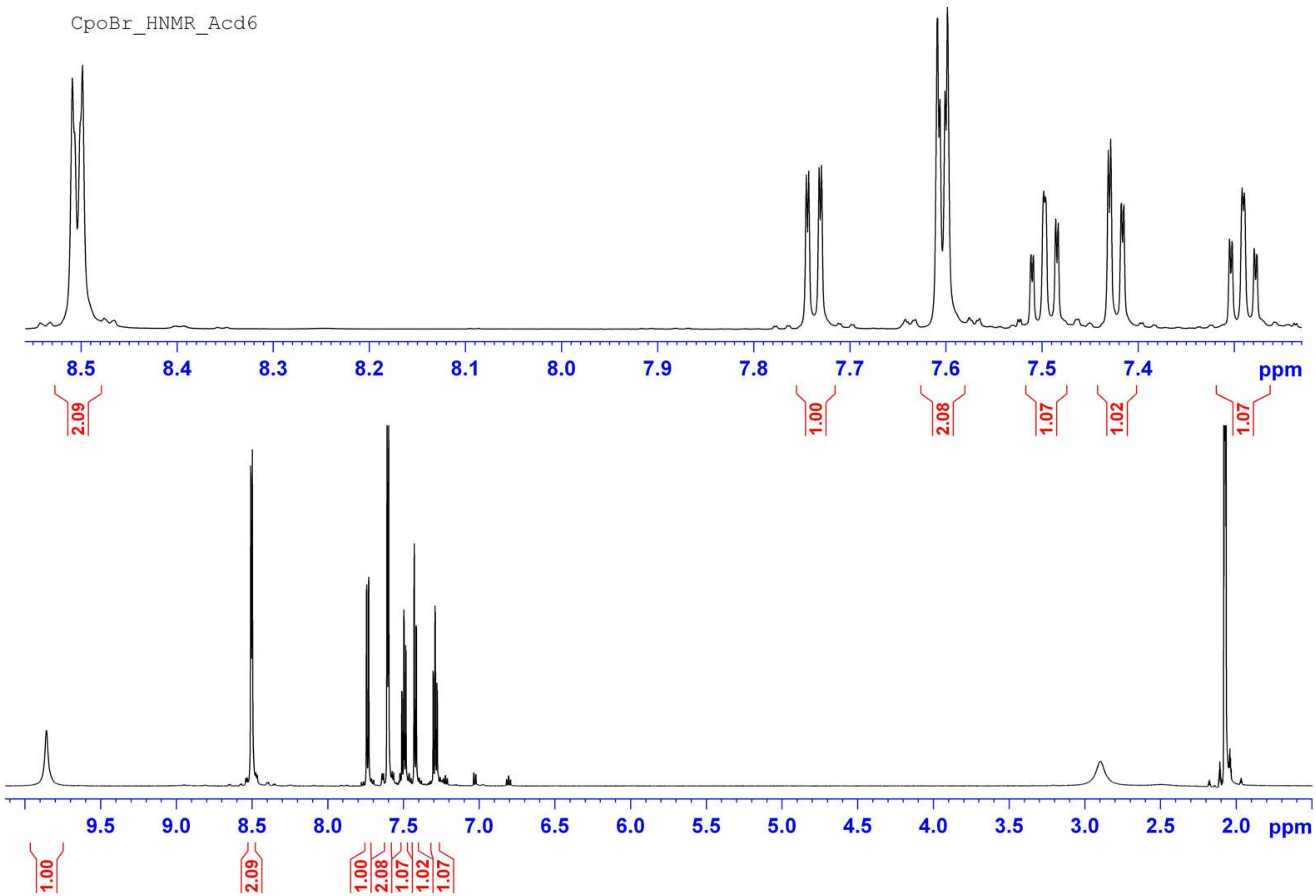


1.3.1.4. **CpmBr** ($CDCl_3$) δ 7.09 (1H, ddd, ^3J = 8.3, ^4J = 2.3, ^5J = 1.0), 7.22 (1H, t, ^3J = 8.1; includes residual $CHCl_3$ solvent), 7.27 (1H, br s), 7.32 (1H, t, ^3J = 2.1), 7.36 (3H, m), 8.46 (2H, d, ^3J = 4.8);

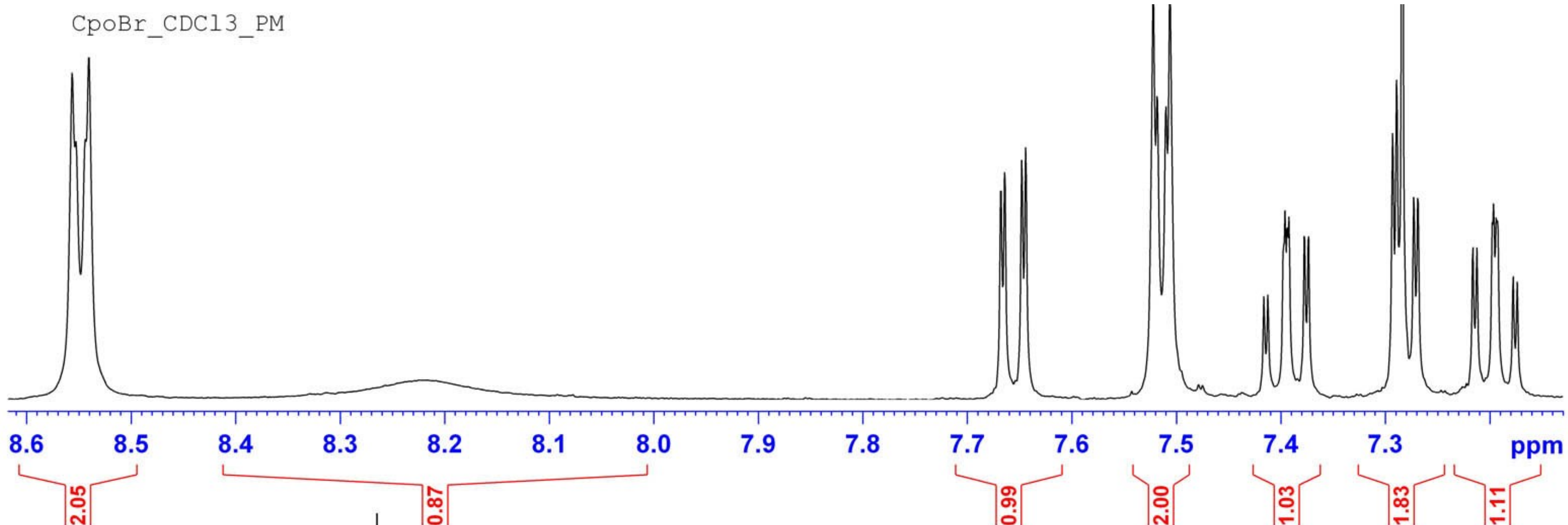


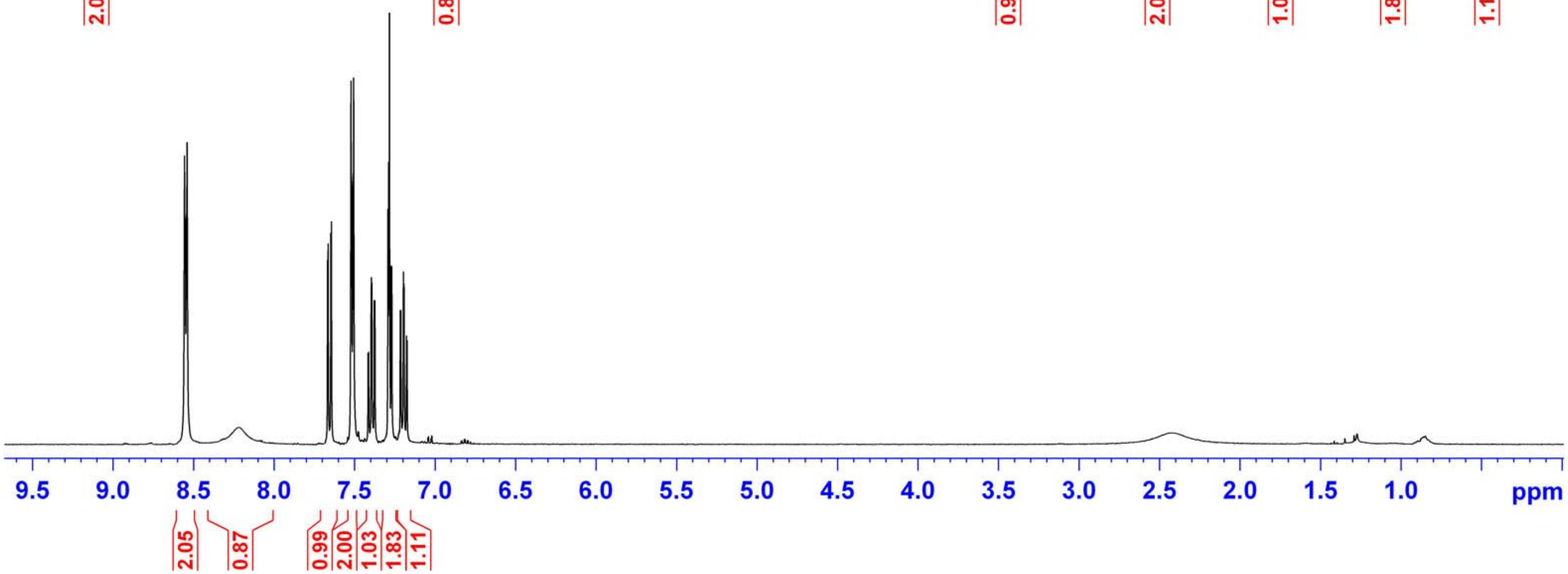


1.3.1.5. **CpoBr** (600 MHz, Acetone-d_6): δ 7.29 (1H, td, ^3J = 7.8, ^4J = 1.5), 7.42 (1H, dd, ^3J = 8.0, ^4J = 1.5), 7.50 (1H, td, ^3J = 7.7, ^4J = 1.3), 7.60 (2H, dd, ^3J = 5.0, ^4J = 1.5), 7.74 (1H, dd, ^3J = 8.0, ^4J = 1.5), 8.50 (2H, dd, , ^3J = 4.8), 9.86 (1H, br s);

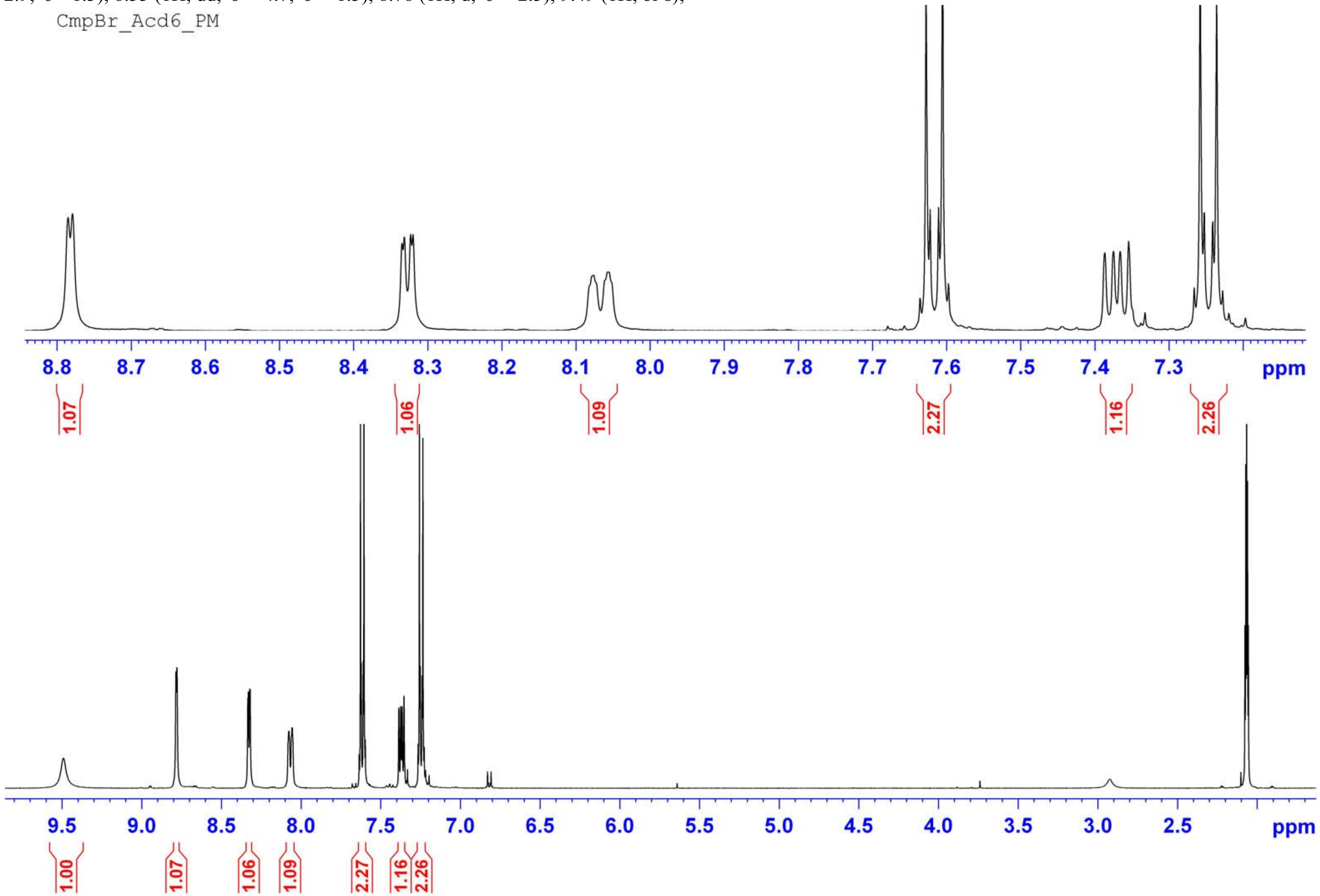


1.3.1.6. **CpoBr** ($CDCl_3$) δ 7.19 (1H, td, ^3J = 7.7, ^4J = 1.6), 7.28 (1H, dd, ^3J = 8.0, ^4J = 1.5; includes $CHCl_3$ residual solvent), 7.39 (1H, ddd, ^3J = 8.5, ^4J = 7.4, ^5J = 1.5), 7.51 (2H, dd, ^3J = 4.6, ^4J = 1.5), 7.66 (1H, dd, ^3J = 8.1, ^4J = 1.5), 8.22 (1H, br s), 8.55 (2H, dd, ^3J = 4.9, ^4J = 1.6);

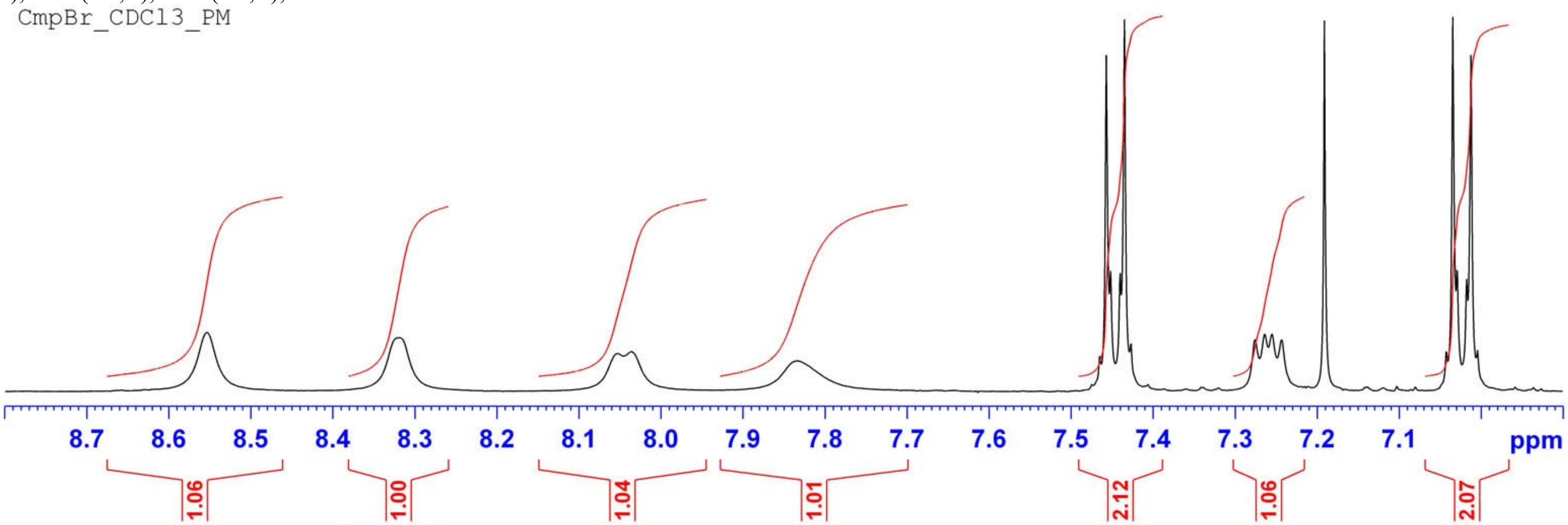


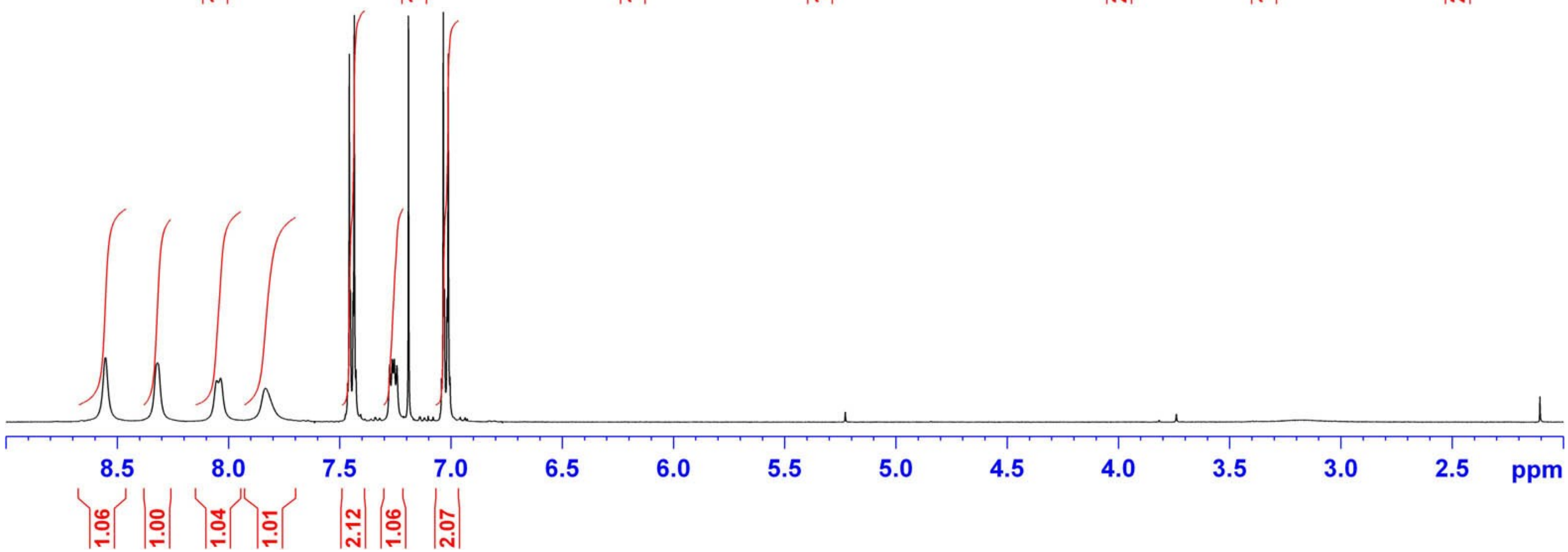


1.3.1.7. **CmpBr** (Acetone-d_6): δ 7.24 (2H, dt, ^3J = 8.8, ^4J = 2.7), 7.37 (1H, dd, ^3J = 8.4, ^4J = 4.7), 7.62 (2H, dt, ^3J = 8.9, ^4J = 2.7), 8.07 (1H, ddd, ^3J = 8.4, ^4J = 2.9, ^5J =1.3), 8.33 (1H, dd, ^3J = 4.7, ^4J = 1.3), 8.78 (1H, d, ^3J = 2.3), 9.49 (1H, br s);

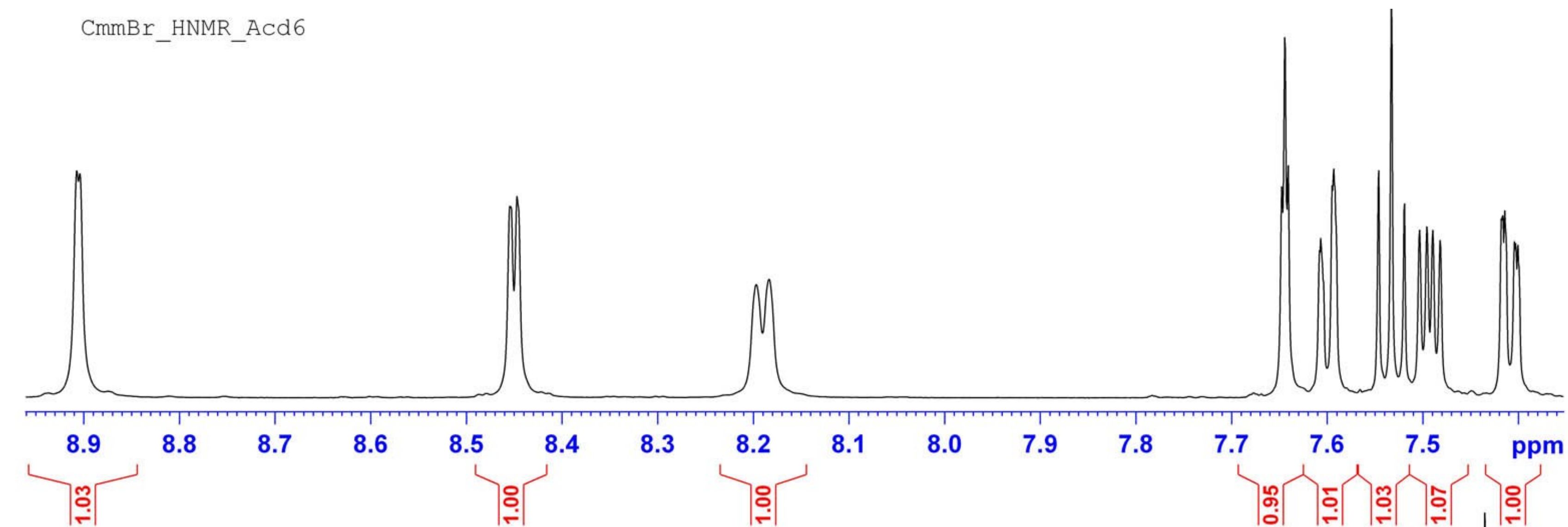


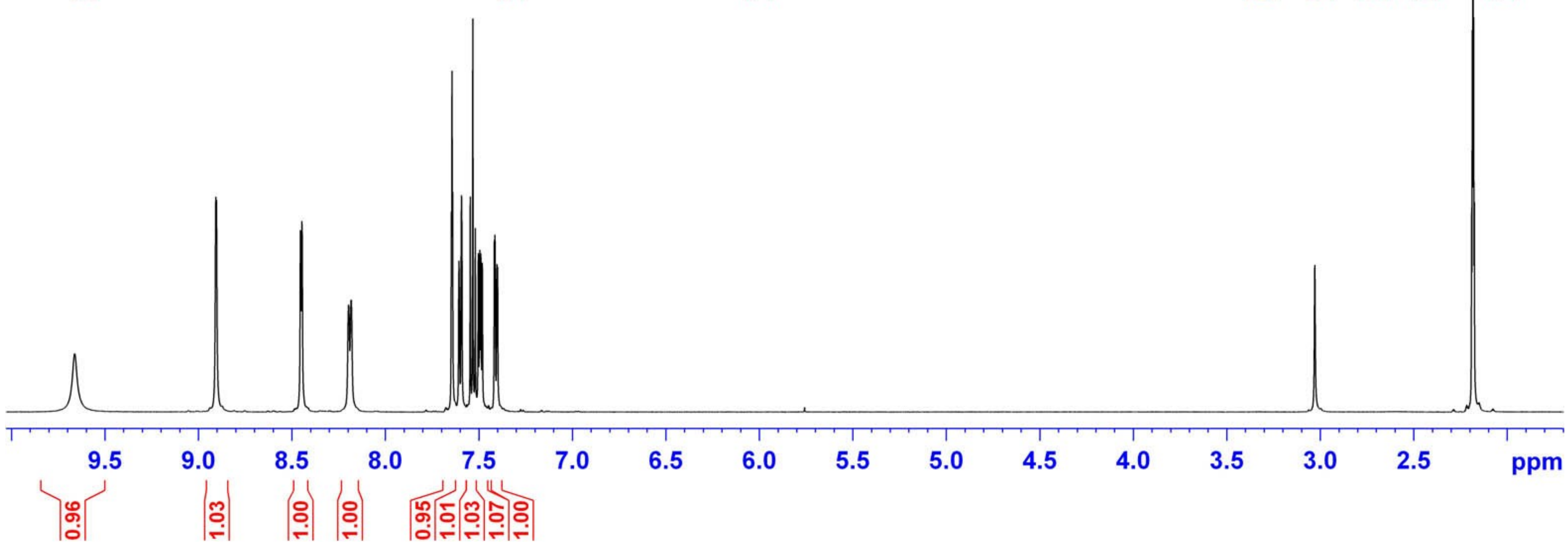
1.3.1.8. **CmpBr** ($CDCl_3$) δ 7.02 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.6), 7.26 (1H, dd, ^{3}J = 8.6, ^{4}J = 4.8), 7.45 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.6); 7.83 (1H, br s), 8.05 (1H, d, ^{3}J = 7.2), 8.32 (1H, s), 8.55 (1H, s);



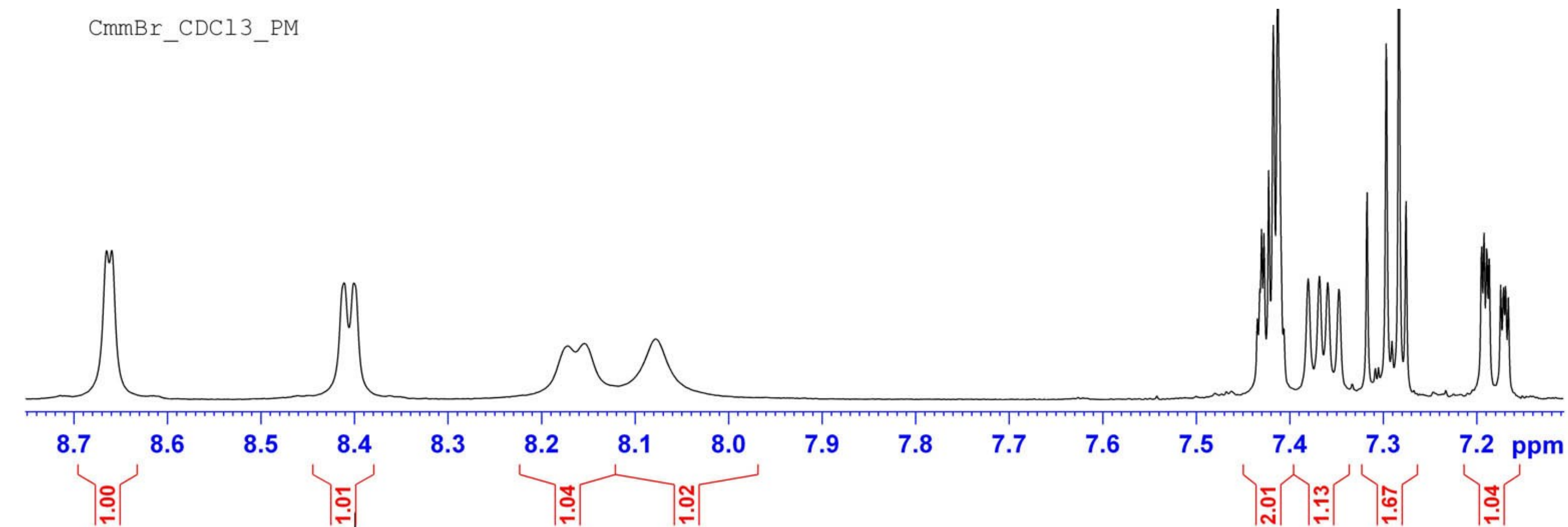


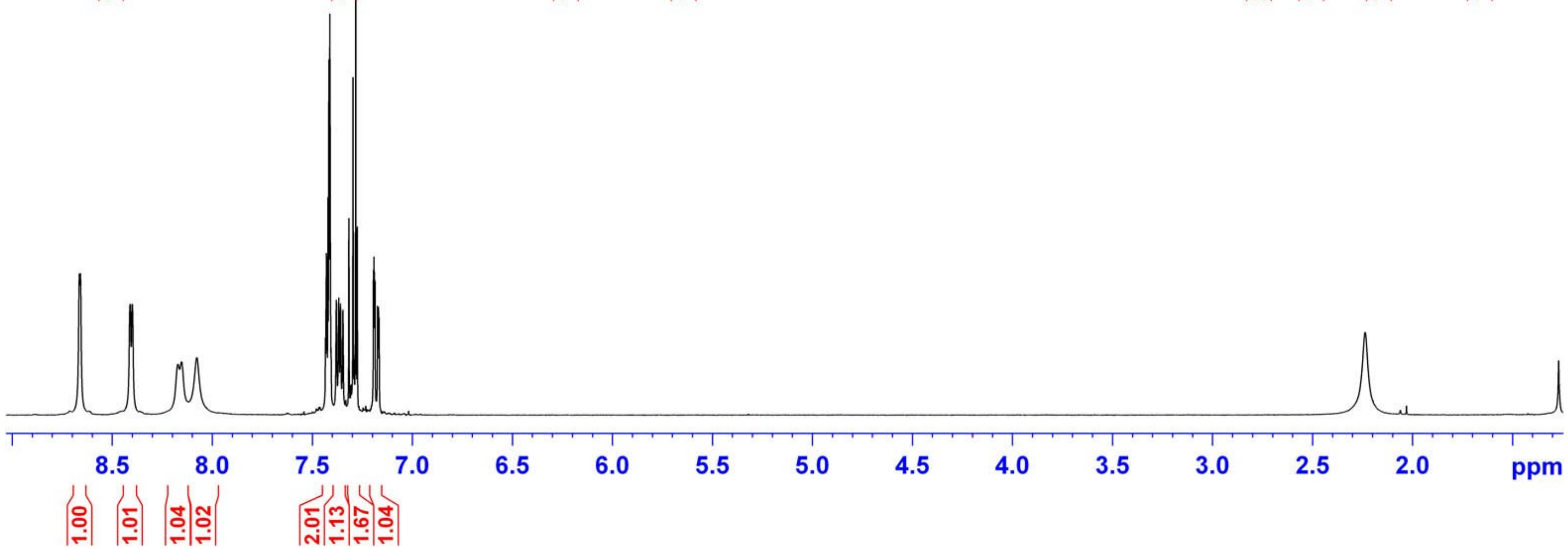
1.3.1.9. **CmmBr** (Acetone-d_6): δ 7.41 (1H, dd, ^3J = 8.3, ^4J = 1.8), 7.49 (1H, dd, ^3J = 8.4, ^4J = 4.6), 7.53 (1H, t, ^3J = 8.0), 7.60 (1H, d, ^3J = 8.0), 7.64 (1H, t, ^3J = 1.8), 8.19 (1H, d, ^3J = 8.1), 8.45 (1H, d, ^3J = 4.8), 8.91 (1H, d, ^3J = 1.9), 9.66 (1H, br s);



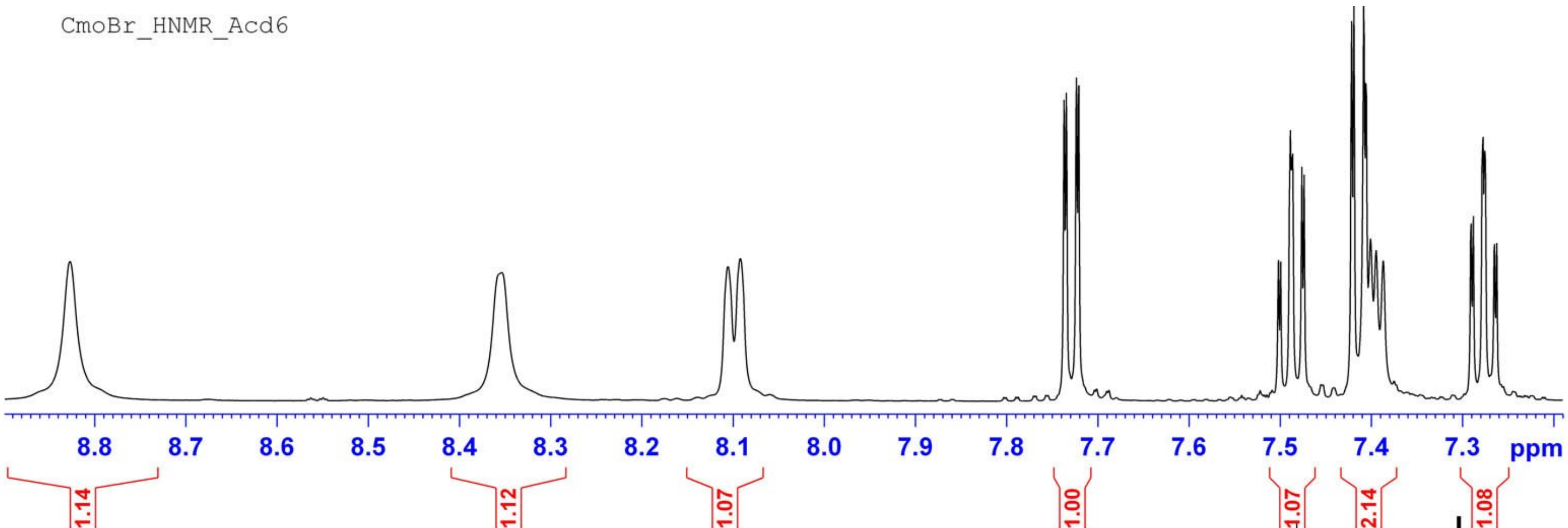


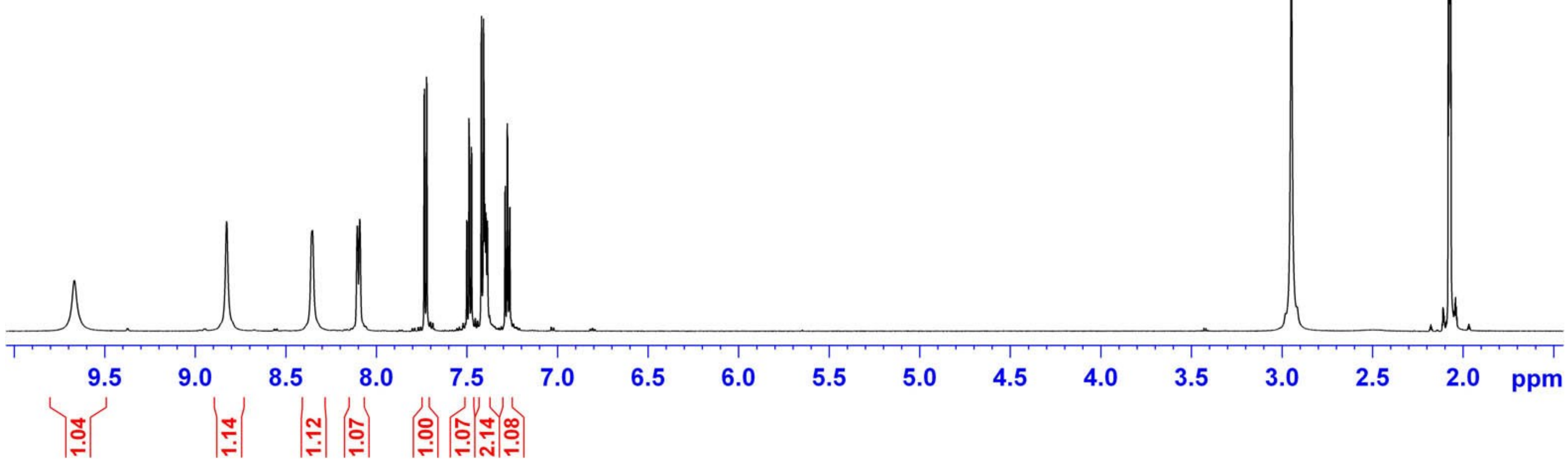
1.3.1.10. **CmmBr** ($CDCl_3$) δ 7.18 (1H, ddd, ^3J = 8.2, ^4J = 2.2, ^5J = 1), 7.30 (1H, t, ^3J = 8.3; includes residual $CHCl_3$ solvent), 7.36 (1H, dd, ^3J = 8.6, ^4J = 4.8), 7.42 (2, m), 8.08 (1H, br s), 8.16 (1H, d, ^3J = 7.0), 8.41 (1H, d, ^3J = 4.4), 8.66 (1H, d, ^3J = 2.3);



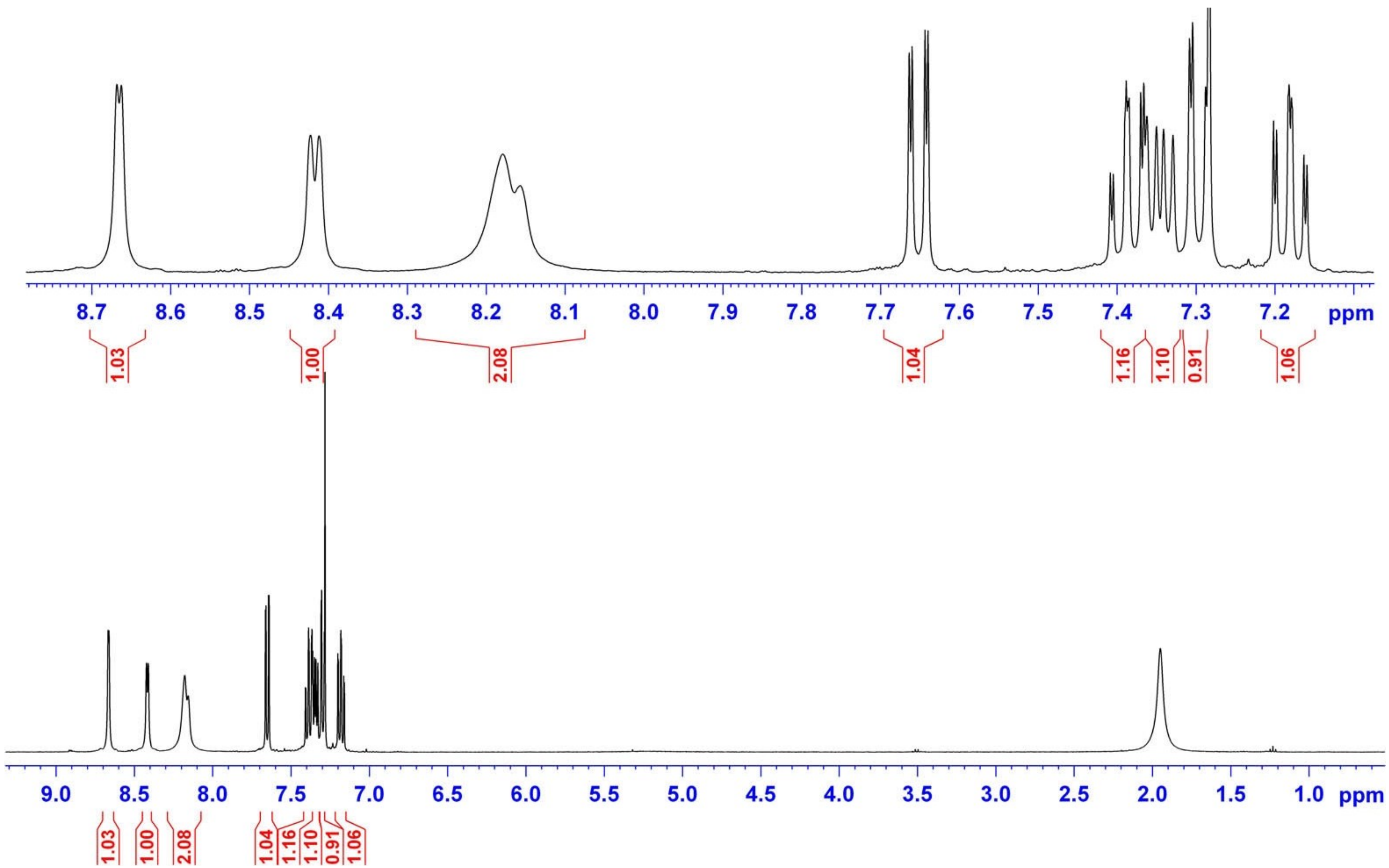


1.3.1.11. **CmoBr** (Acetone-d_6): δ 7.27 (1H, td, ^3J = 7.7, ^4J = 1.5), 7.40 (1H, dd, ^3J = 8.2, ^4J =4.6), 7.41 (1H, dd, ^3J = 8.1, ^4J = 1.5), 7.49 (1H, ddd, ^3J = 8.4, ^4J = 7.8, ^5J = 1.4), 7.73 (1H, dd, ^3J = 8.0, ^4J = 1.5), 8.10 (1H, d, ^3J = 8.1), 8.35 (1H, s), 8.83 (1H, s), 9.67 (1H, br s);

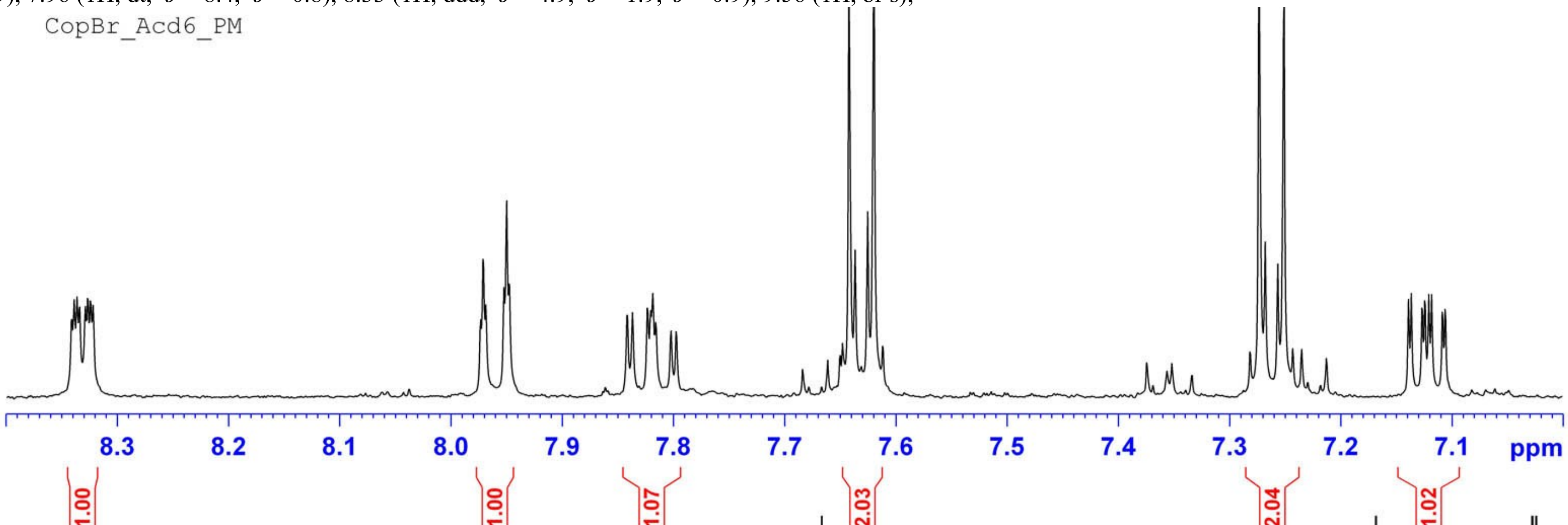


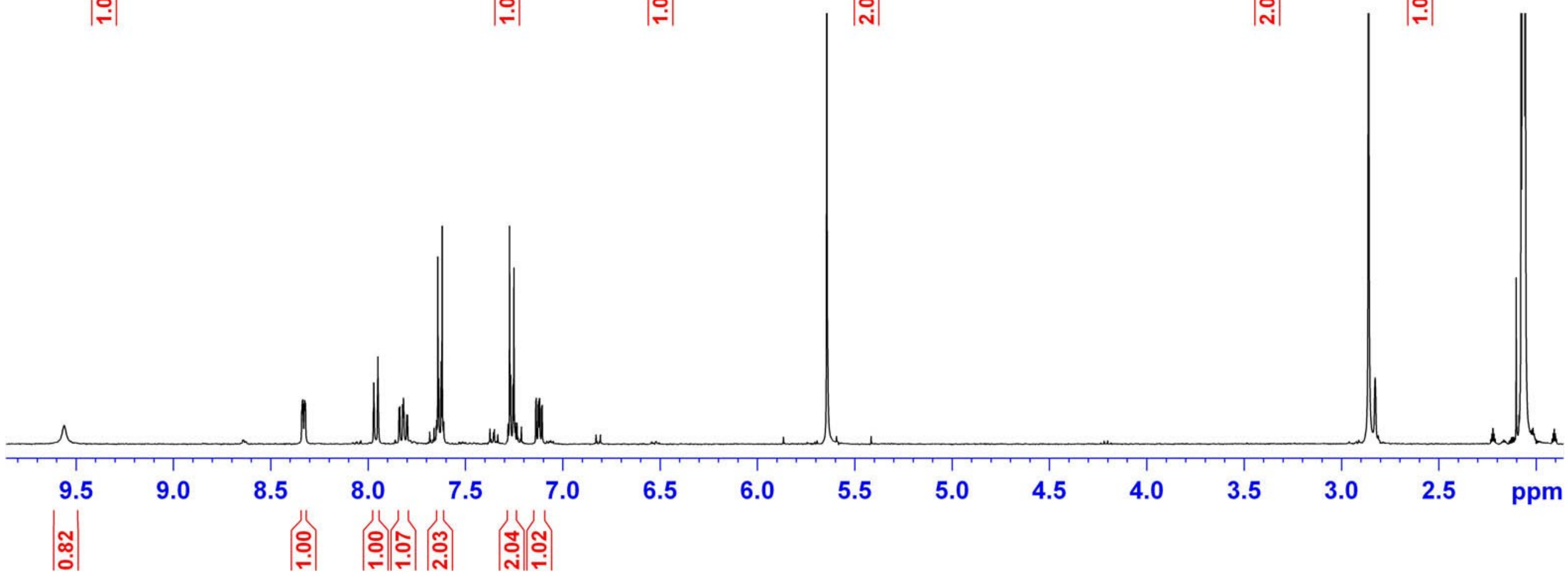


1.3.1.12. **CmoBr** ($CDCl_3$) δ 7.18 (1H, td, ^{3}J = 7.7, ^{4}J = 1.6), 7.30 (1H, dd, ^{3}J = 8.0, ^{4}J = 1.5), 7.35 (1H, dd, ^{3}J = 8.2, ^{4}J = 4.8), 7.39 (1H, ddd, ^{3}J = 8.5, ^{4}J = 7.7, ^{5}J = 1.5), 7.65 (1H, dd, ^{3}J = 8.0, ^{4}J = 1.4), 8.16 (1H, d, ^{3}J = 8.0), 8.18 (1H, br s), 8.42 (1H, d, ^{3}J = 4.3), 8.67 (1H, d, ^{3}J = 2.2);



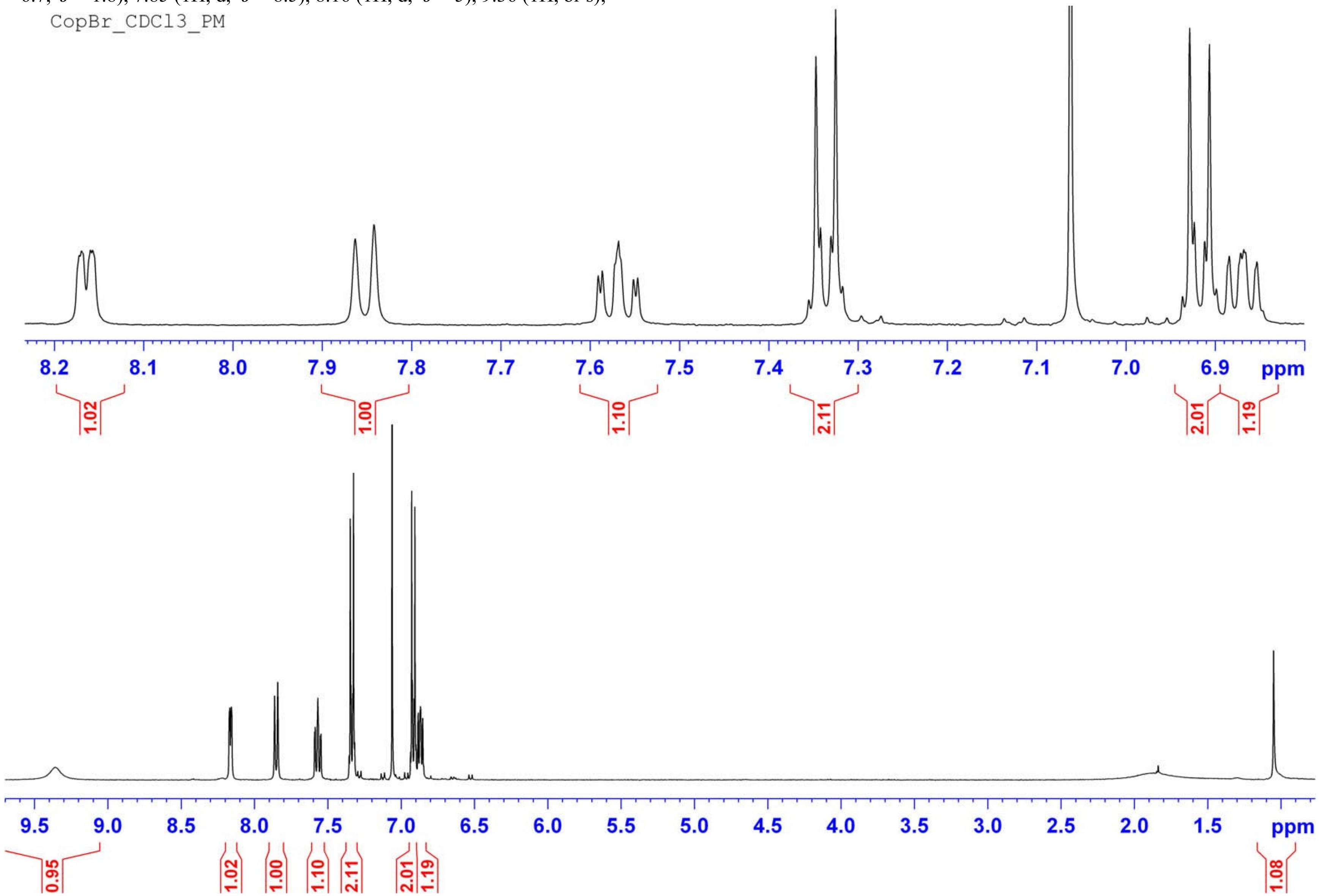
CopBr (Acetone-d_6): δ 7.12 (1H, ddd, ^{3}J = 7.6, ^{4}J = 4.9, ^{5}J = 1.0), 7.26 (2H, dt, ^{3}J = 8.9, ^{4}J = 2.2), 7.63 (2H, dt, ^{3}J = 9.0, ^{4}J = 2.2), 7.82 (1H, ddd, ^{3}J = 8.3, ^{4}J = 7.0, ^{5}J = 1.9), 7.96 (1H, dt, ^{3}J = 8.4, ^{4}J = 0.8), 8.33 (1H, ddd, ^{3}J = 4.9, ^{4}J = 1.9, ^{5}J = 0.9), 9.56 (1H, br s);



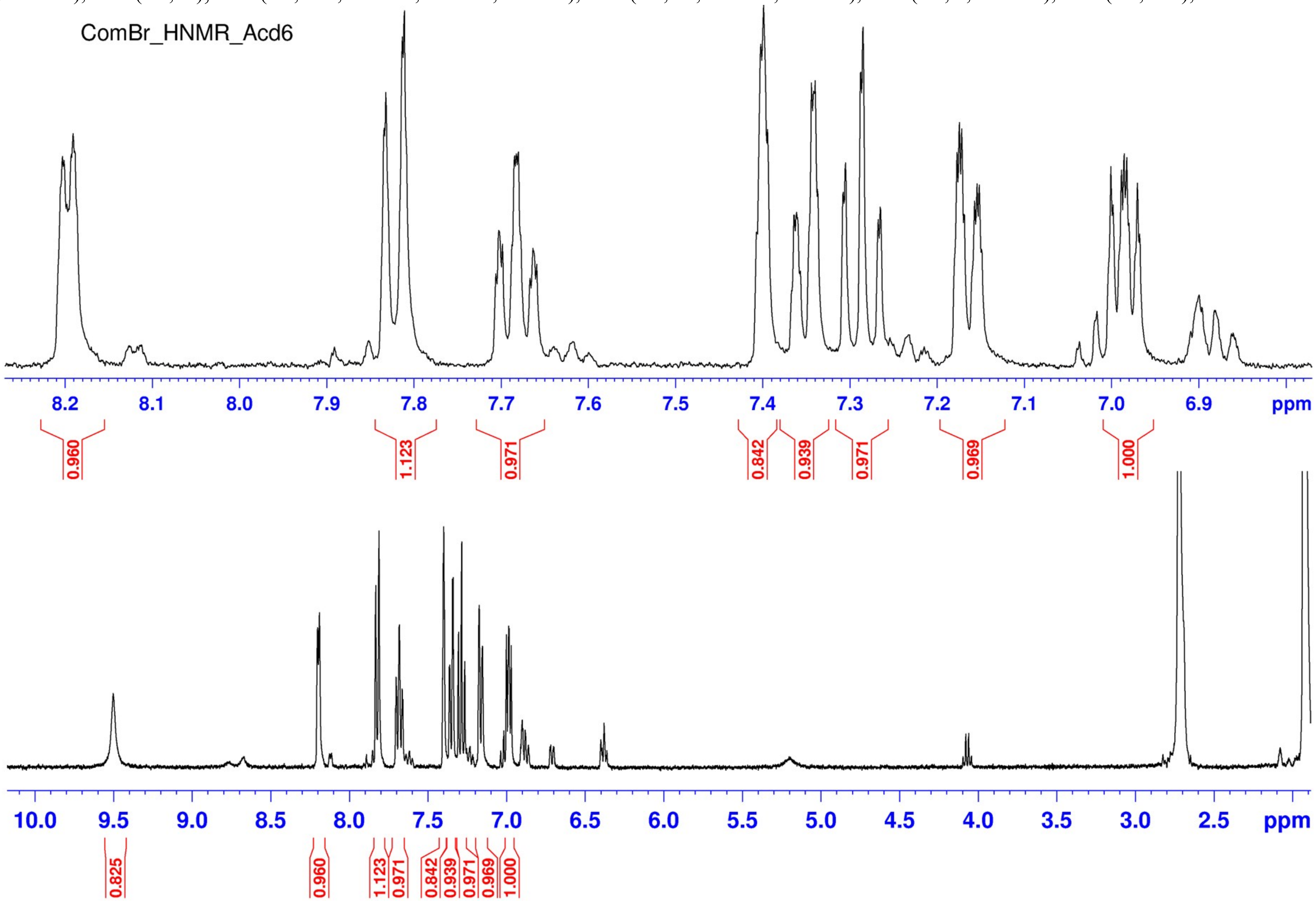


1.3.1.13.

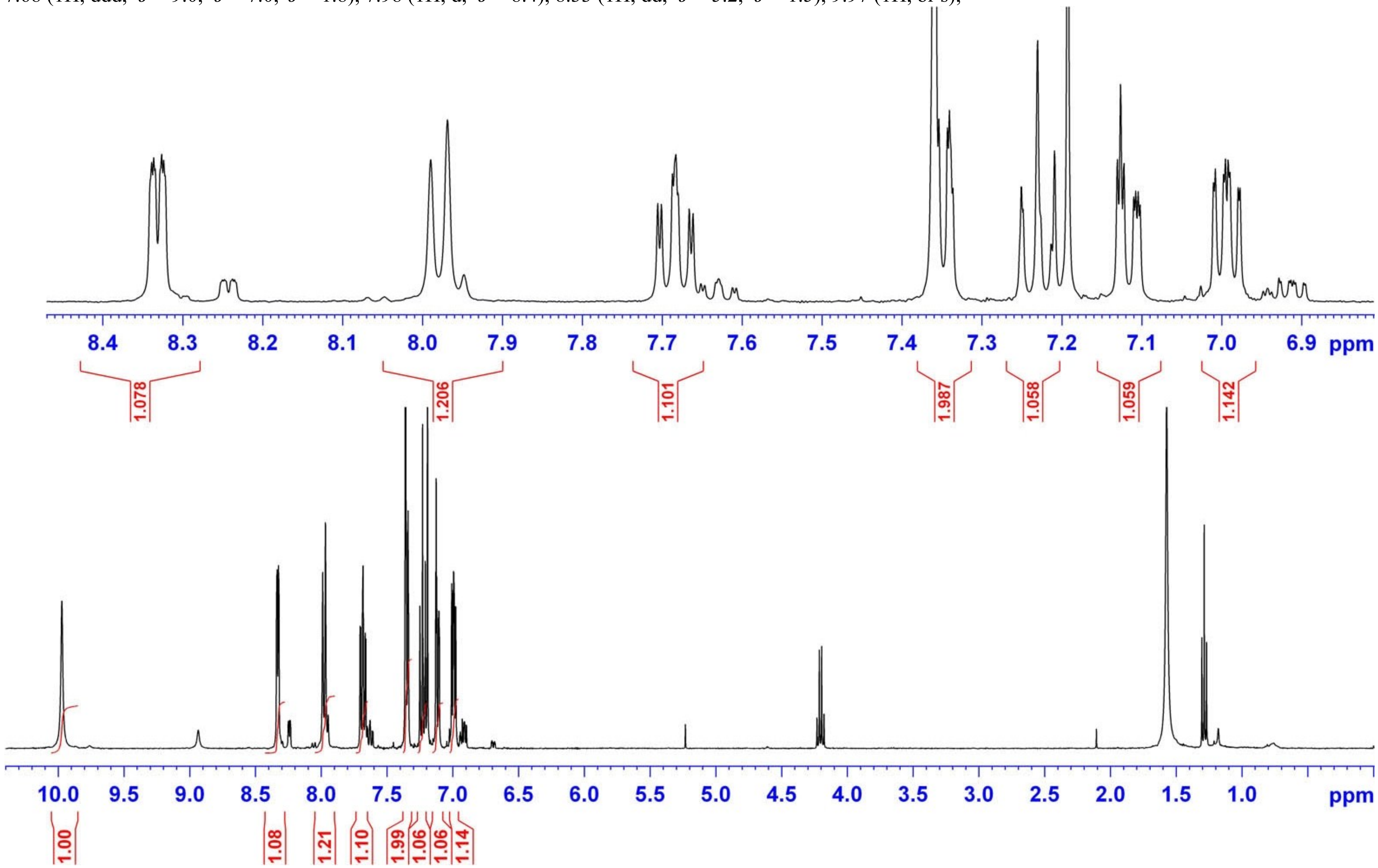
1.3.1.14. **CopBr** ($CDCl_3$) δ 6.87 (1H, ddd, ^3J = 7.6, ^4J = 5.1, ^5J = 0.7), 6.92 (2H, dt, ^3J = 8.9, ^4J = 2.5), 7.34 (2H, dt, ^3J = 8.8, ^4J = 2.5), 7.57 (1H, ddd, ^3J = 8.6, ^4J = 6.7, ^5J = 1.8), 7.85 (1H, d, ^3J = 8.5), 8.16 (1H, d, ^3J = 5), 9.36 (1H, br s);



1.3.1.15. **ComBr** (Acetone-d_6) δ 6.99 (1H, ddd, ^3J = 7.3, ^4J = 5.0, ^5J = 0.1), 7.16 (1H, ddd, ^3J = 8.1, ^4J = 2.0, ^5J = 1.1), 7.28 (1H, td, ^3J = 8.1, ^4J = 0.9), 7.35 (1H, d, ^3J = 8.6), 7.40 (1H, m), 7.68 (1H, ddd, ^3J = 8.7, ^4J = 7.5, ^5J = 1.3), 7.82 (1H, dd, ^3J = 8.3, ^5J = 0.9), 8.20 (1H, d, ^3J = 4.6), 9.50 (1H, br s);

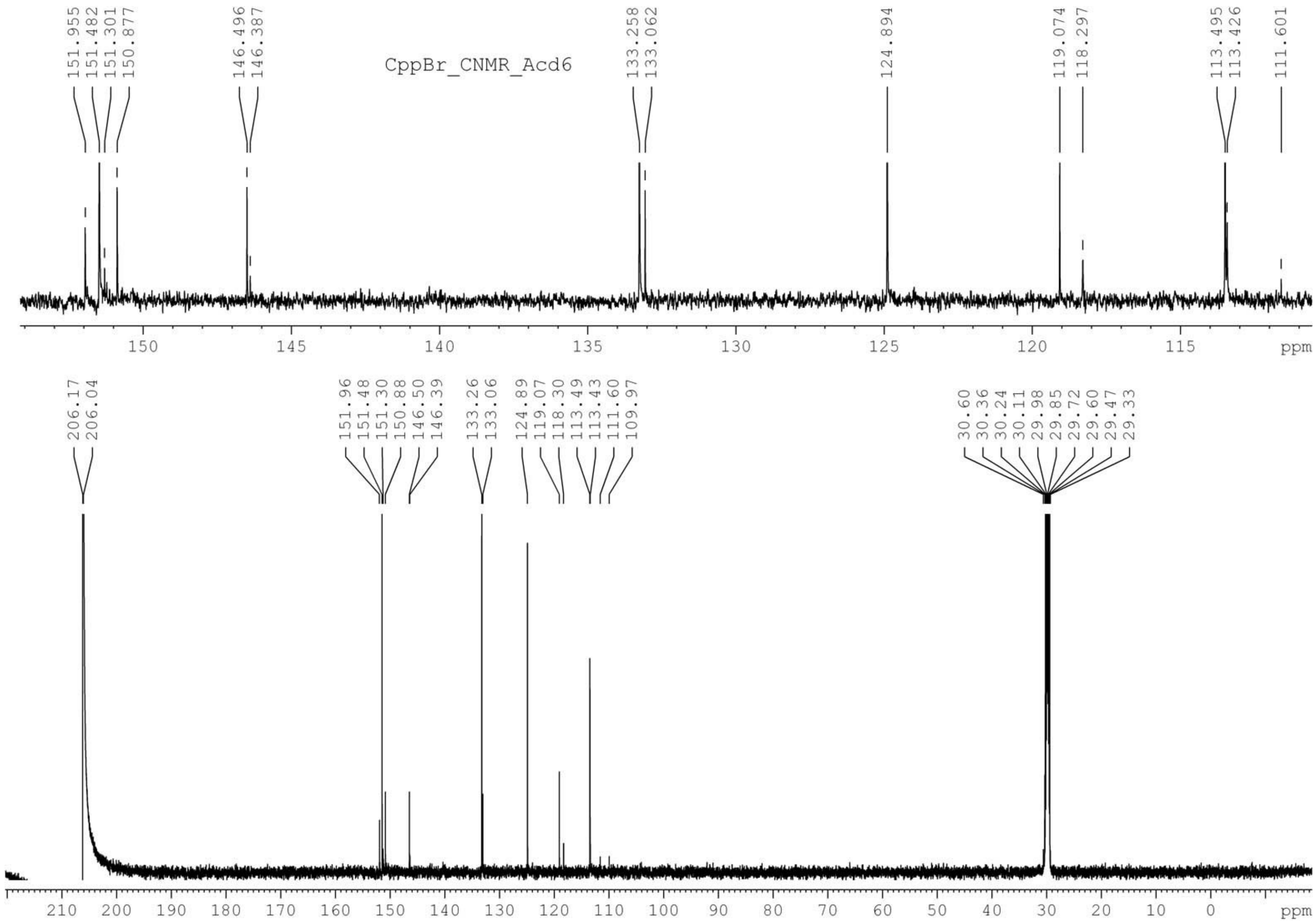


1.3.1.16. **ComBr** ($CDCl_3$) δ 6.99 (1H, ddd, ^{3}J = 7.5, ^{4}J = 5.0, ^{5}J = 0.8), 7.12 (1H, ddd, ^{3}J = 8.2, ^{4}J = 2.2, ^{5}J = 1.0), 7.23 (1H, td, ^{3}J = 8.2, ^{4}J = 0.9), 7.37 (2H, m), 7.68 (1H, ddd, ^{3}J = 9.0, ^{4}J = 7.0, ^{5}J = 1.8), 7.98 (1H, d, ^{3}J = 8.4), 8.33 (1H, dd, ^{3}J = 5.2, ^{4}J = 1.5), 9.97 (1H, br s);

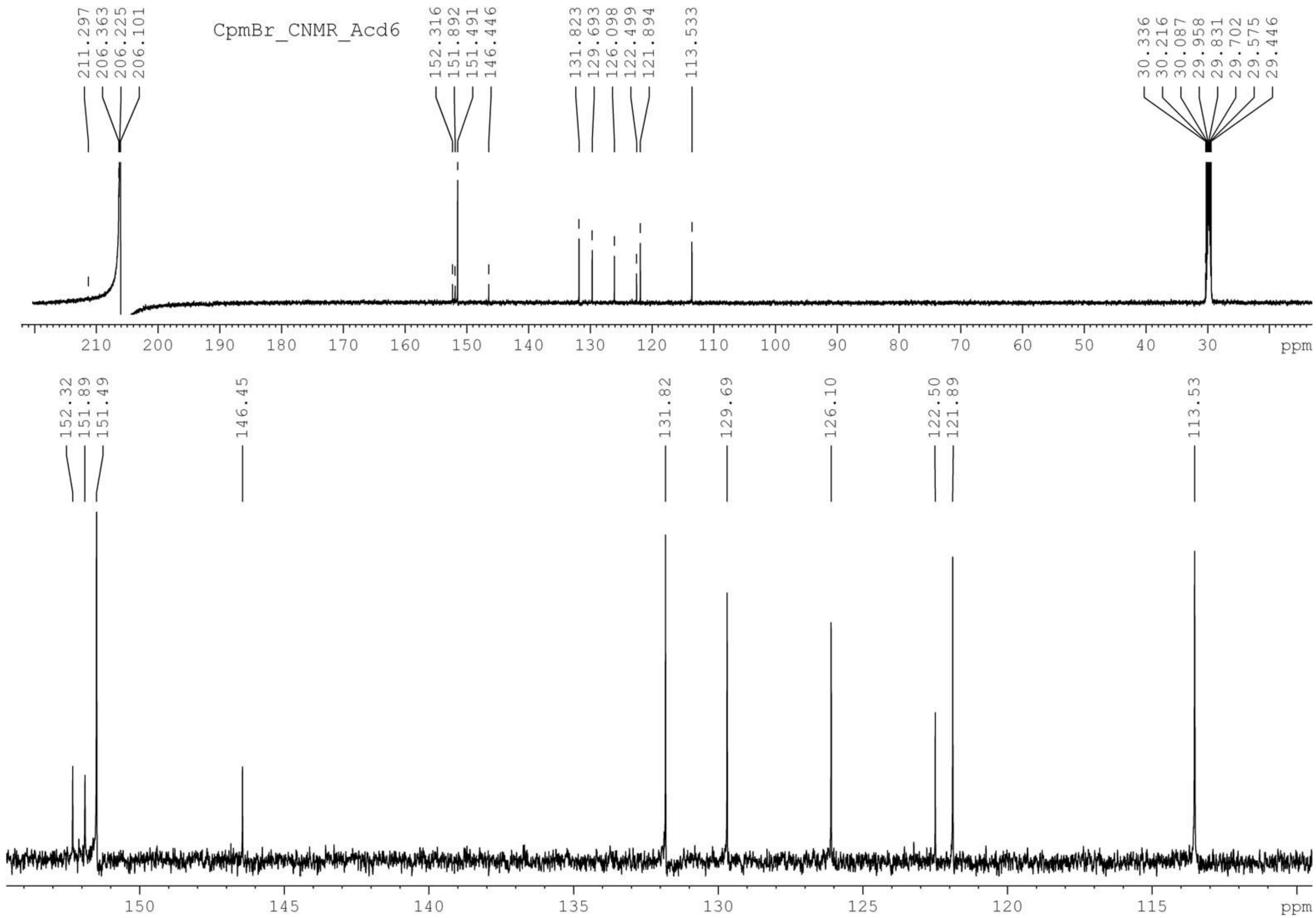


1.3.2. ^{13}C NMR data and spectra (400 MHz, Acetone-d_6)

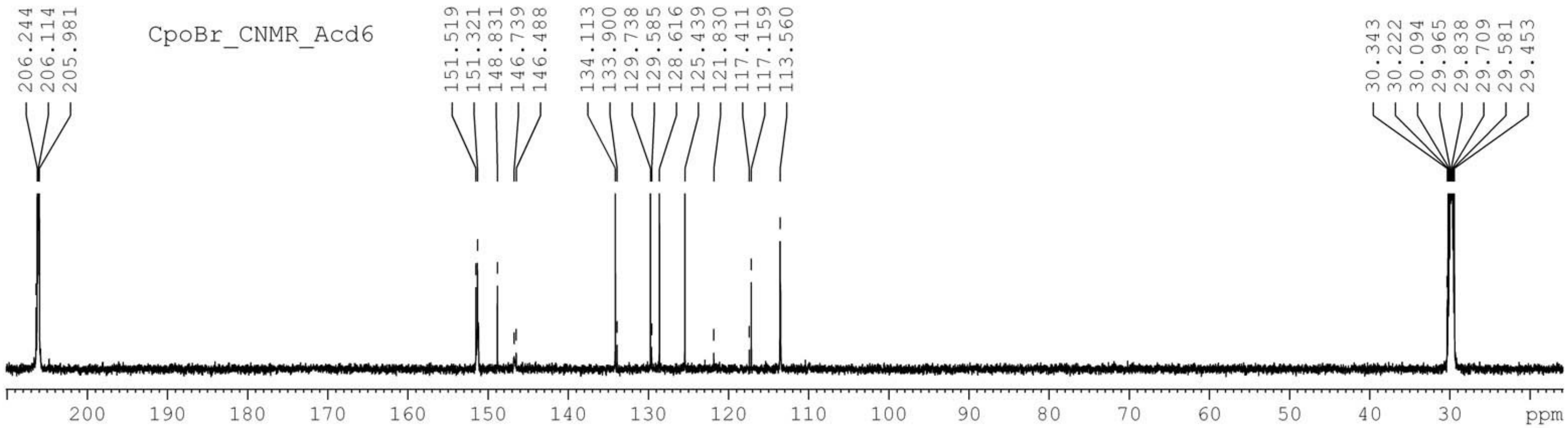
1.3.2.1. **CppBr**: δ 113.50, 119.08, 124.90, 133.26, 146.50, 150.88, 151.49, 151.96;

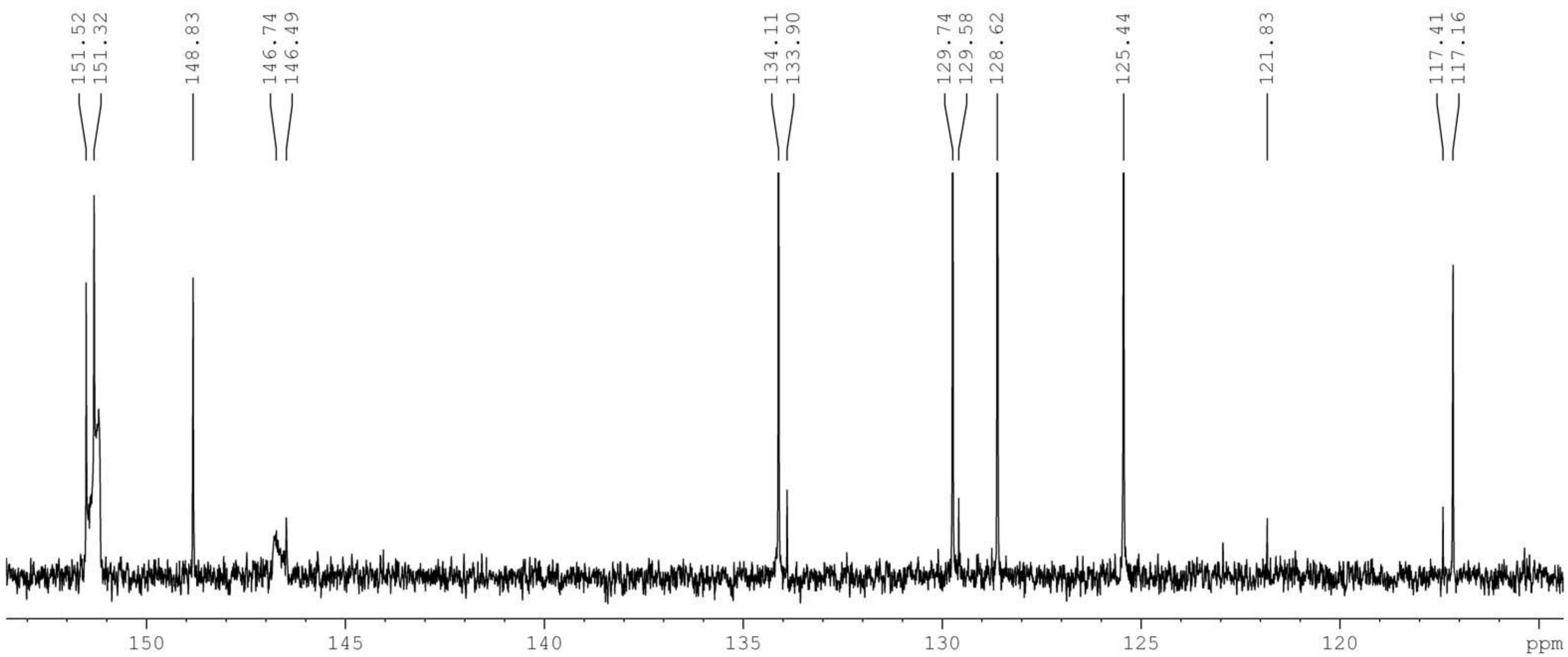


1.3.2.2. **CpmBr**: δ 113.53, 121.89, 122.50, 126.10, 129.69, 131.82, 146.45, 151.49, 151.89, 152.32;

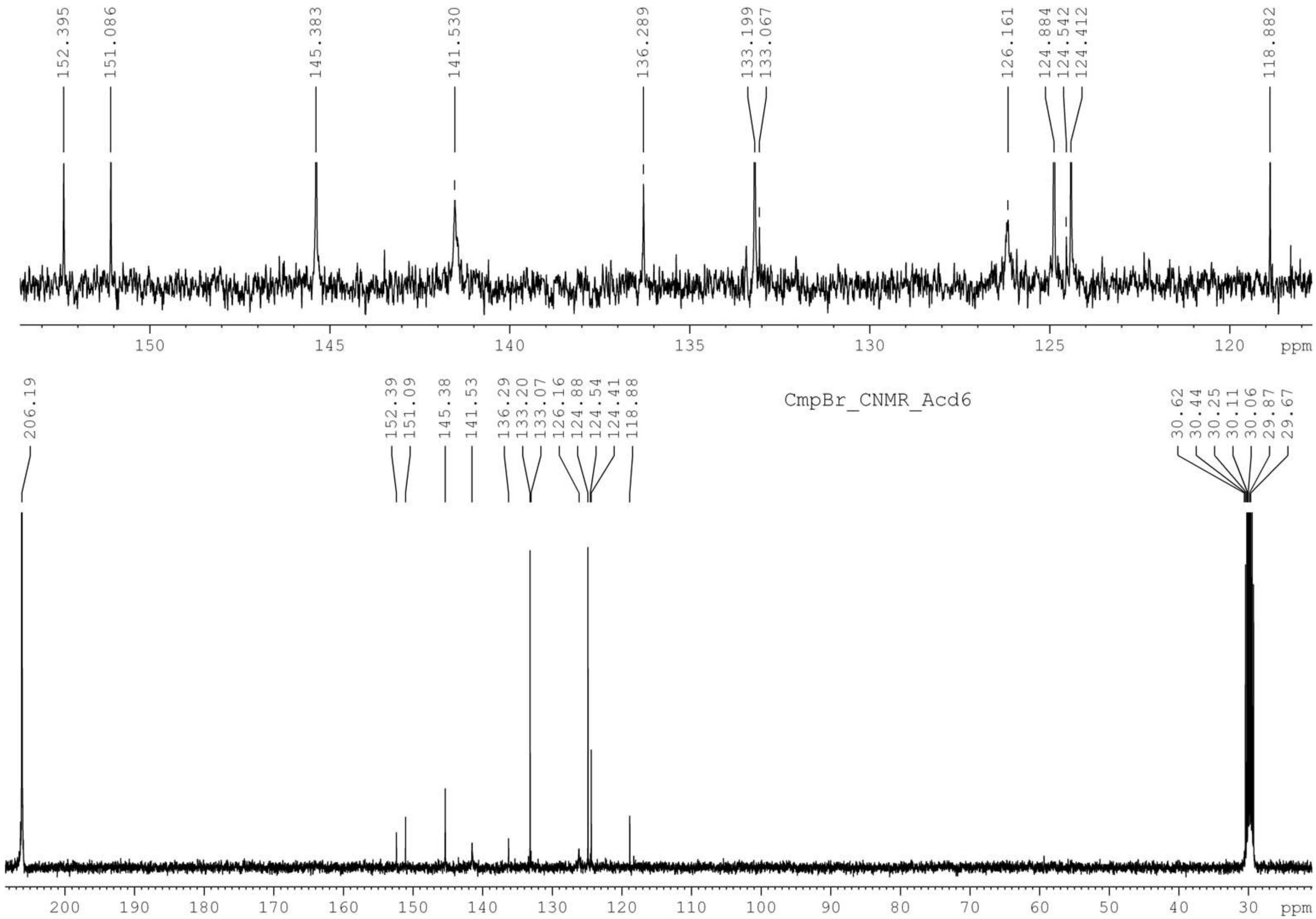


1.3.2.3. **CpoBr**: δ 117.16, 125.44, 128.62, 129.74, 134.11, 146.74, 148.83, 151.32, 151.52

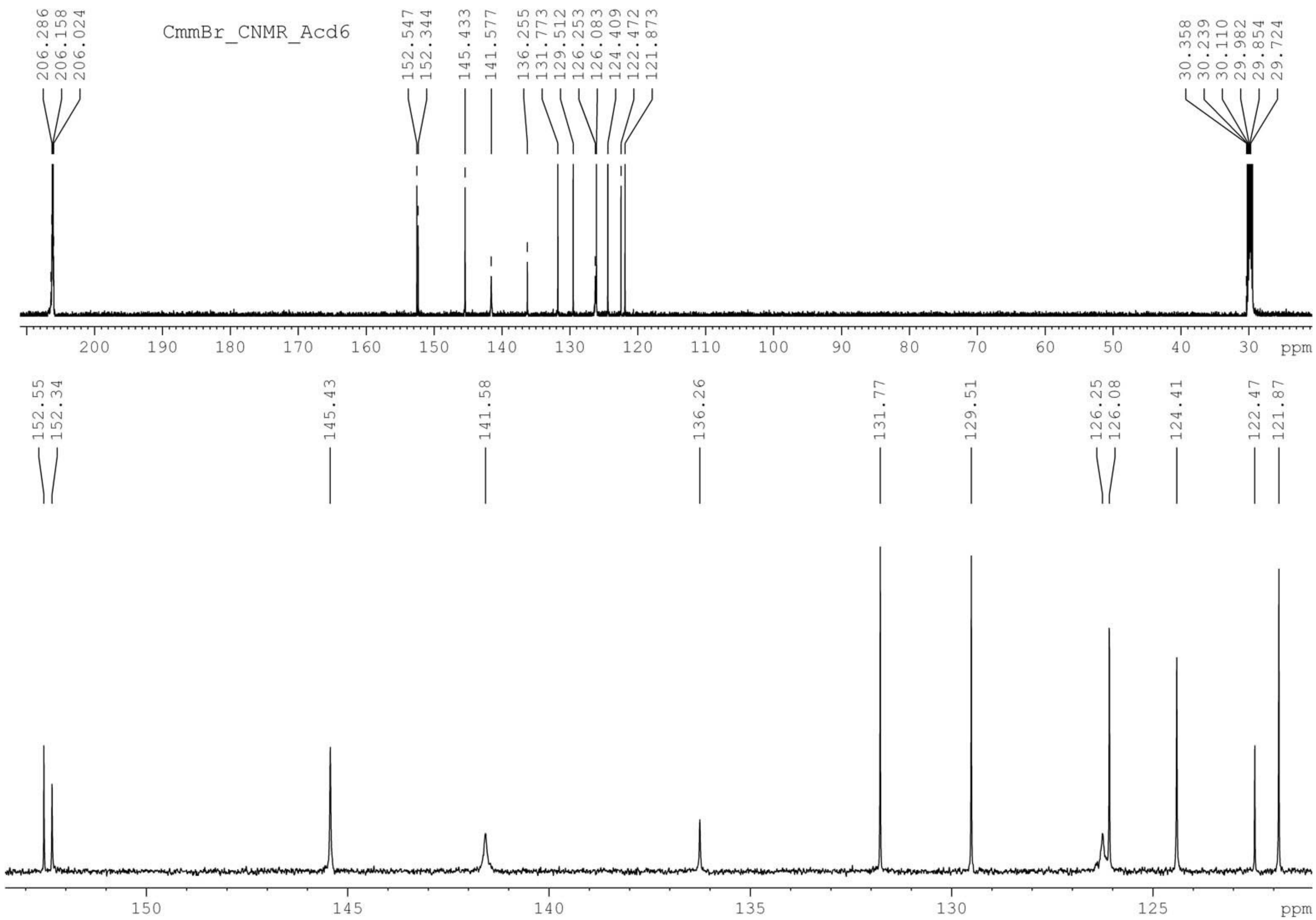




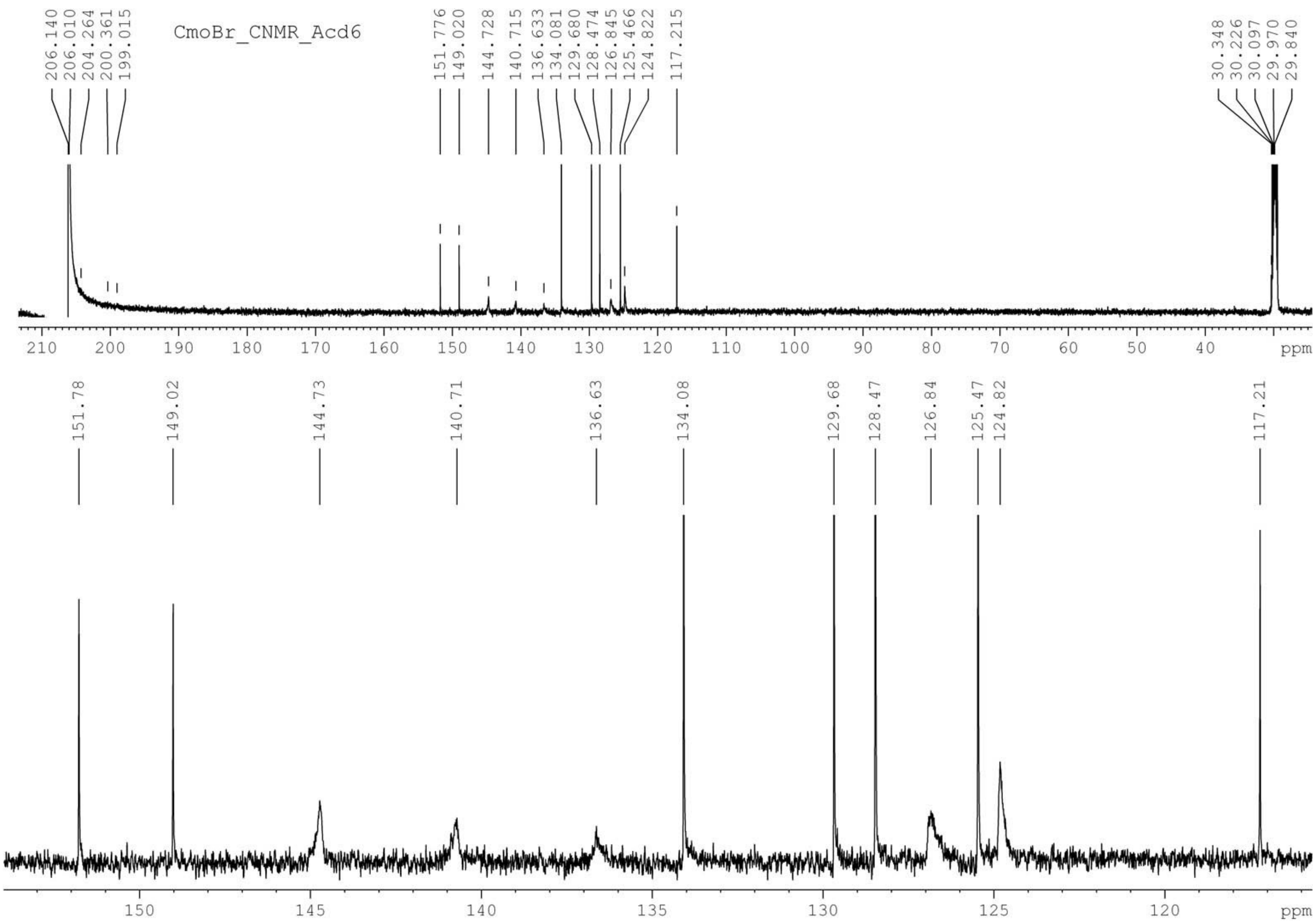
1.3.2.4. **CmpBr** δ 118.88, 124.41, 124.88, 126.18, 133.20, 136.29, 141.52, 145.38, 151.09, 152.39;



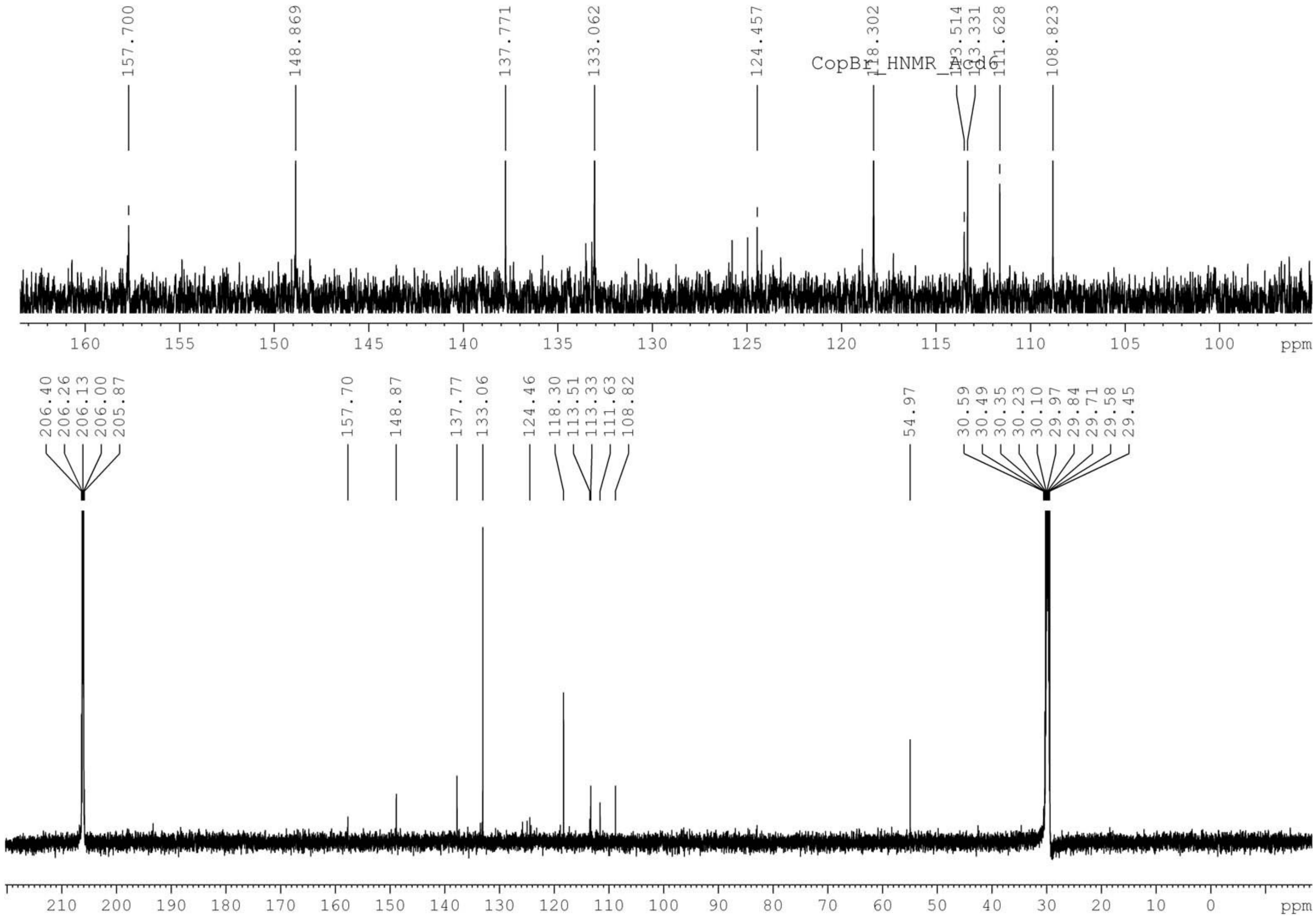
1.3.2.5. **CmmBr**: δ 121.87, 122.47, 124.41, 126.08, 126.25, 129.51, 131.77, 136.26, 141.58, 145.43, 152.34, 152.55;



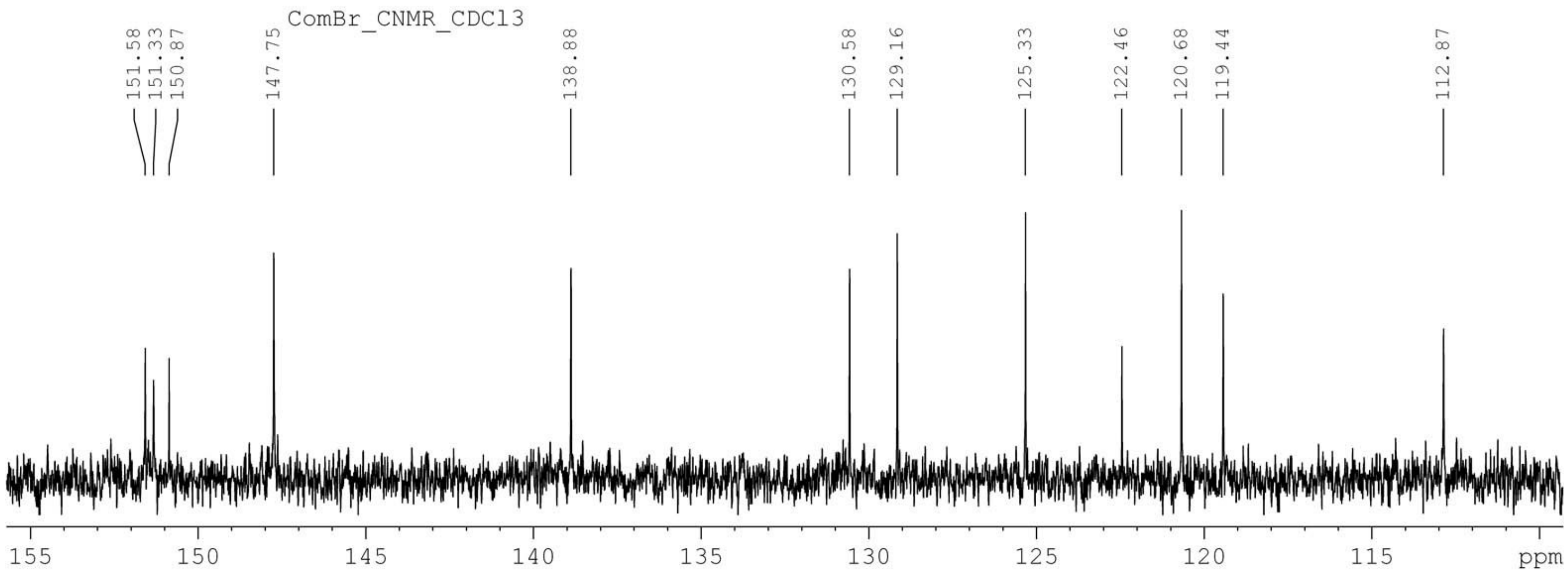
1.3.2.6. **CmoBr**: δ 117.21, 124.82, 125.47, 126.84, 128.47, 129.68, 134.08, 136.63, 140.71, 144.73, 149.02, 151.78;

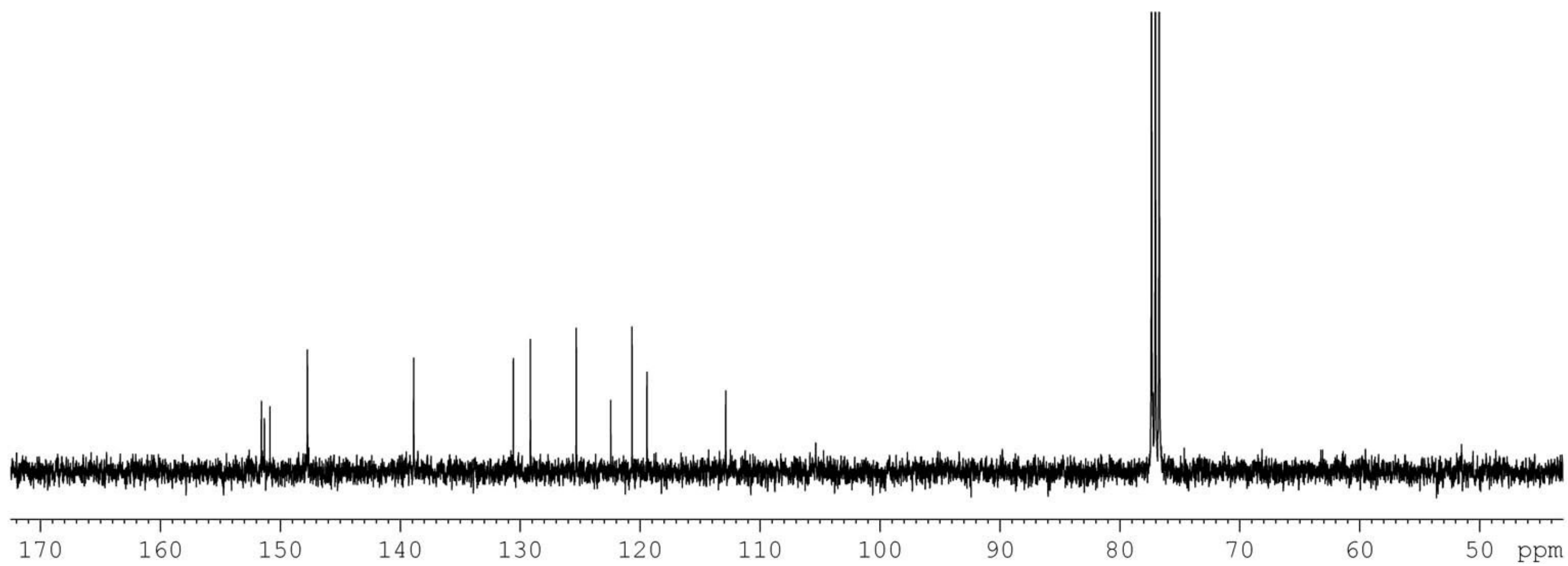


1.3.2.7. **CopBr**: δ 108.82, 111.63, 113.33, 113.51, 118.30, 124.46, 133.06, 137.77, 148.87, 157.70;



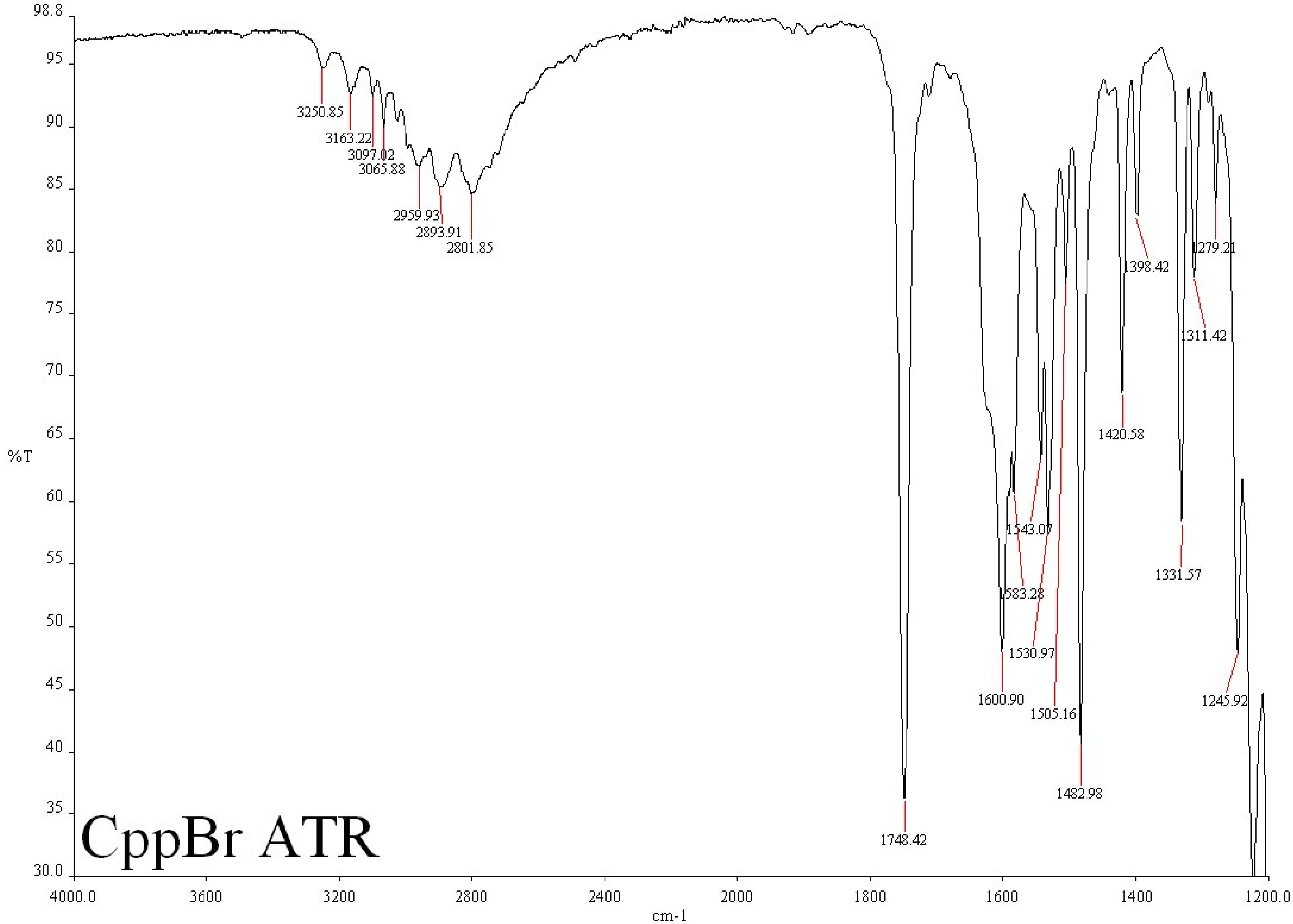
1.3.2.8. **ComBr** ($CDCl_3$): δ 112.87, 119.44, 120.68, 122.46, 125.33, 129.16, 130.58, 138.88, 147.75, 150.87, 151.33, 151.58;



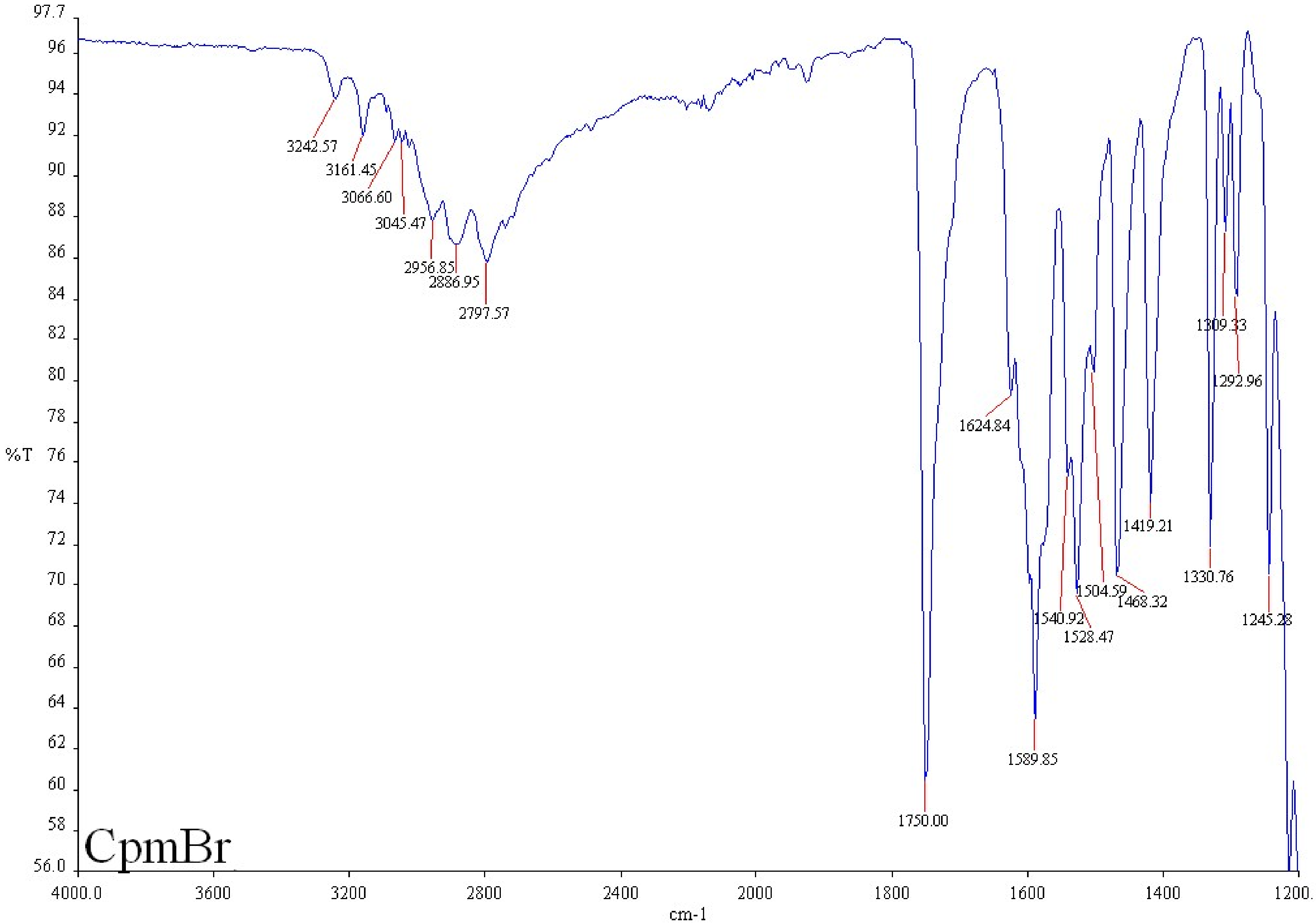


1.3.3. <u>IR (ATR) data and spectra</u>

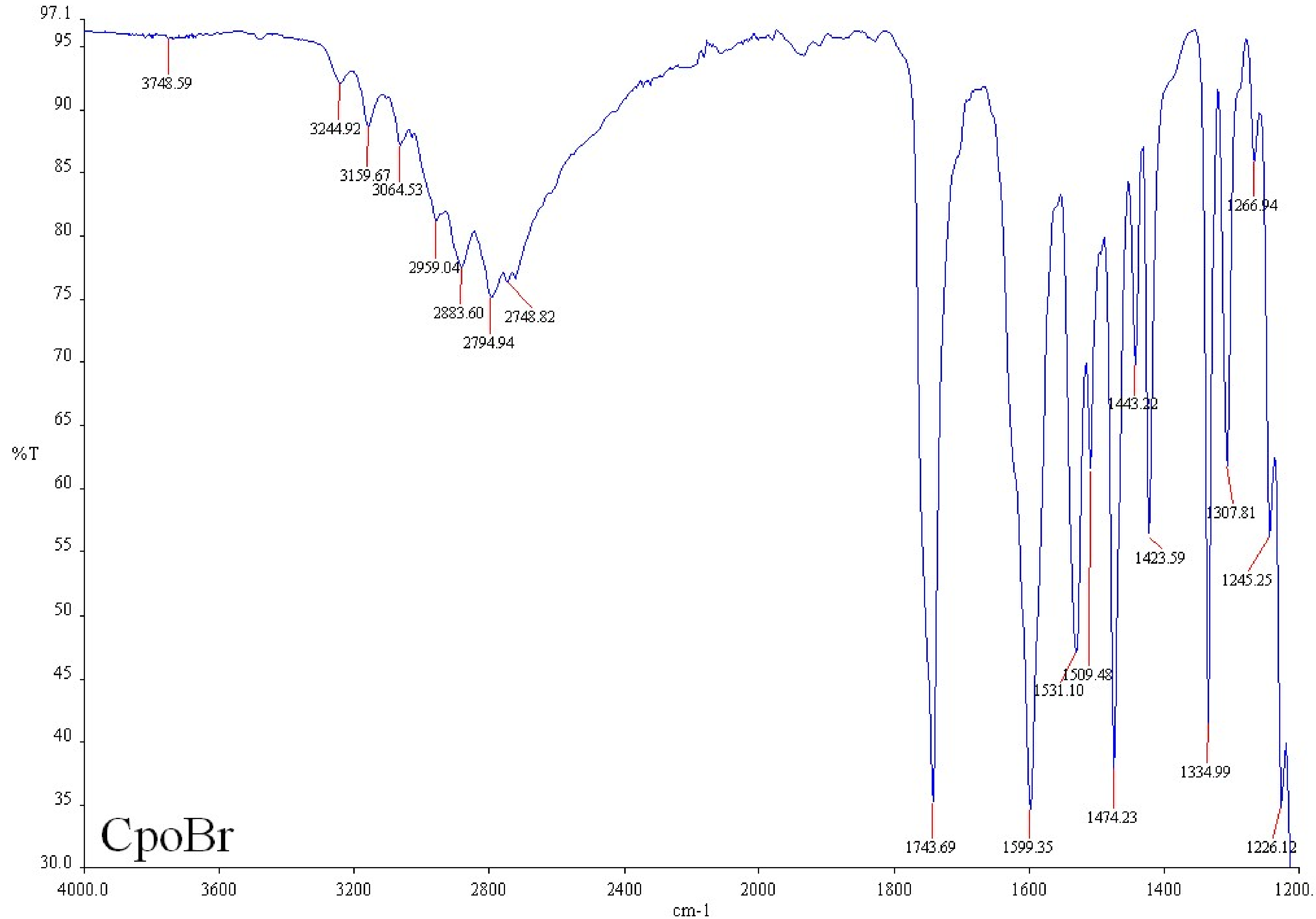
1.3.3.1. **CppBr**: 3251 (w), 3163 (w), 3066 (w), 2960 (w), 2894 (w), 2802 (w), 1748 (s), 1601 (s), 1583 (m), 1543 (m), 1531 (s), 1505 (w), 1483 (s), 1420 (w).



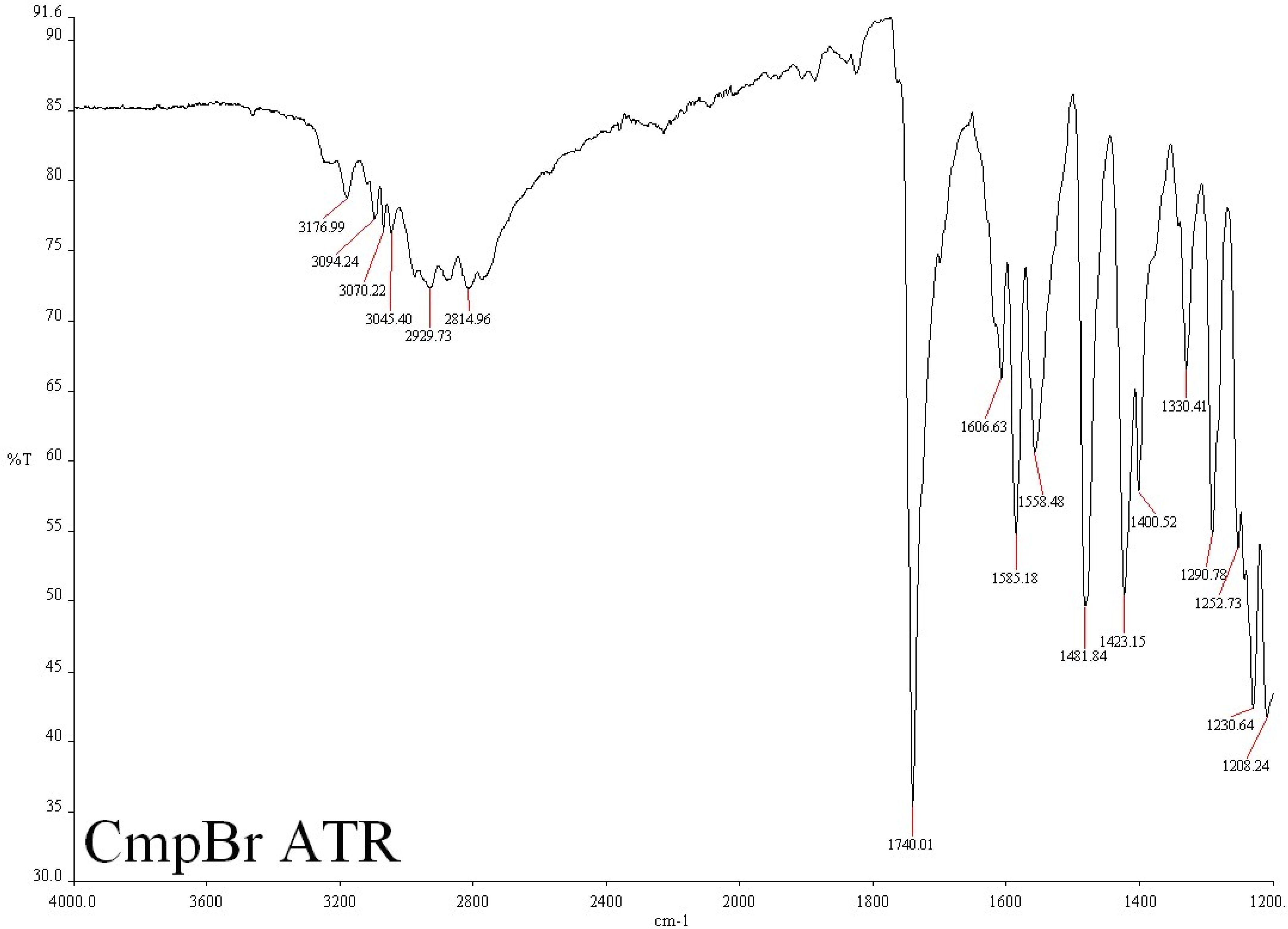
1.3.3.2. **CpmBr:** 3243 (w), 3161 (w), 3067 (w), 2957 (m), 2887 (m), 2798 (m), 1750 (m), 1625 (m), 1590 (s), 1541 (s), 1528 (s), 1505 (m), 1468 (s), 1419 (s).



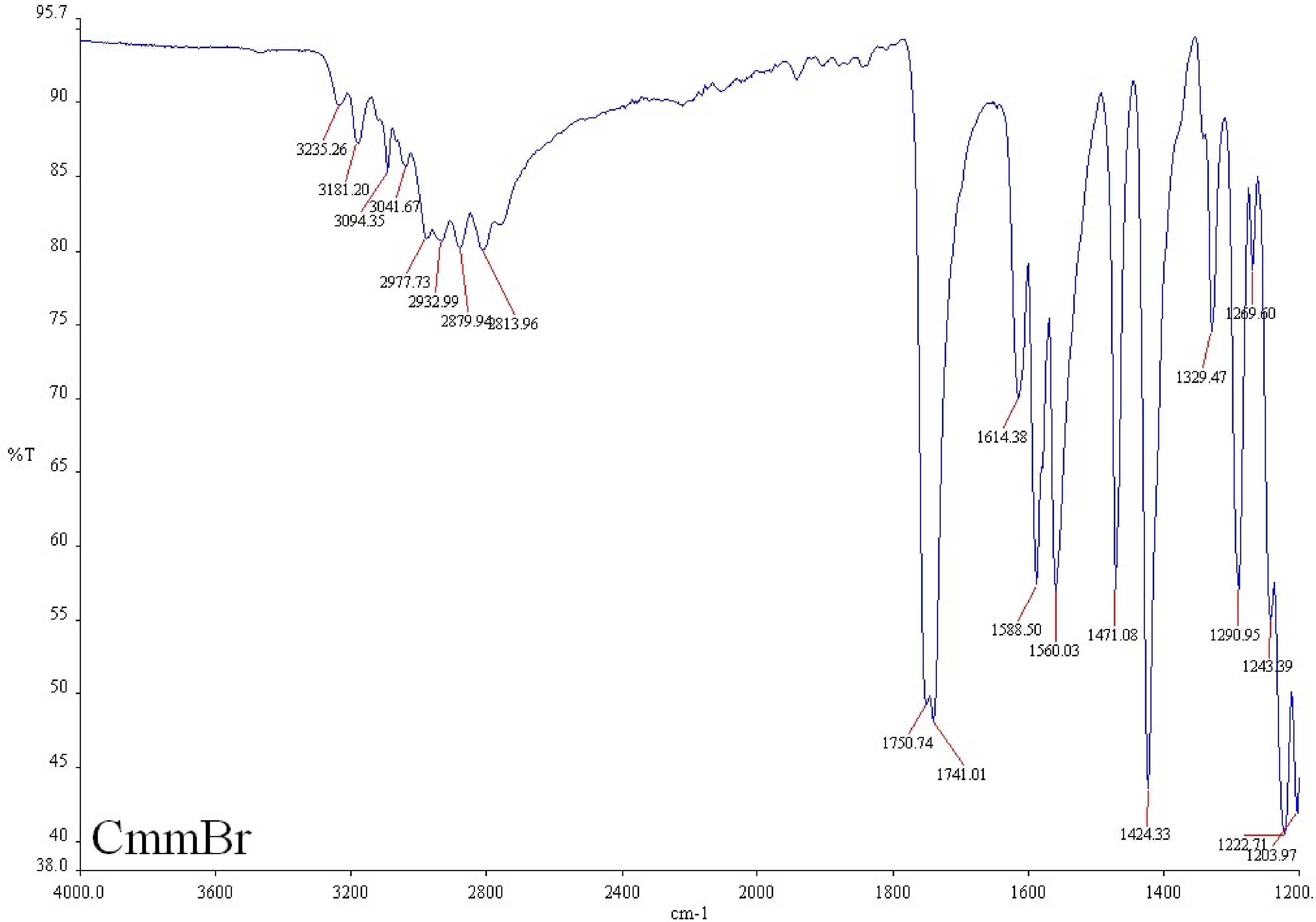
1.3.3.3. **CpoBr**: 3245 (w), 3160 (w), 3064 (w), 2959 (m), 2884 (m), 2795 (m), 1744 9 (s), 1599 (s), 1531 (s), 1509 (m), 1474 (s), 1443 (m), 1424 (s).



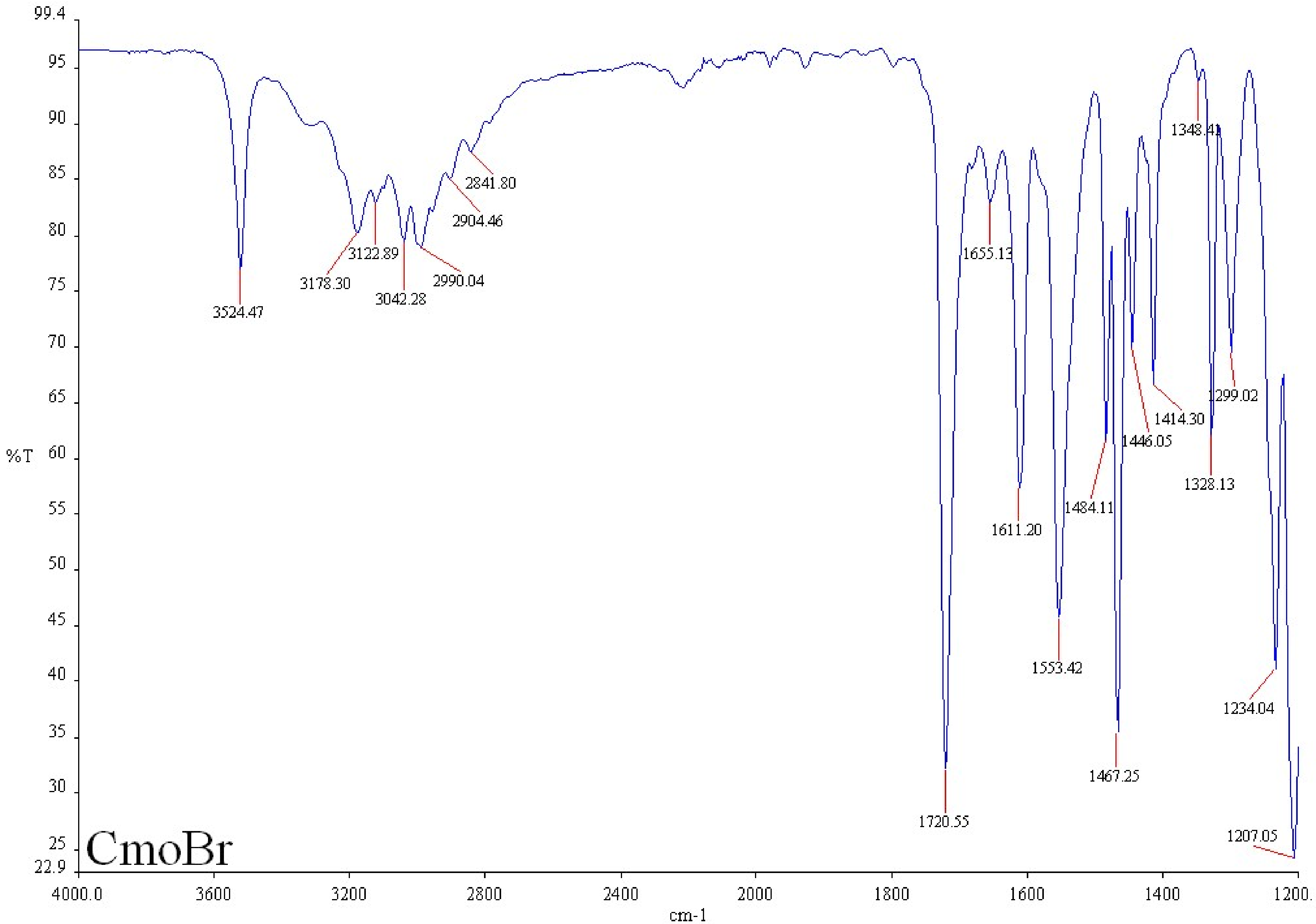
1.3.3.4. **CmpBr**: 3177 (w), 3094 (w), 3070 (w), 3045 (w), 2930 (w), 2815 (w), 1740 (s), 1607 (m), 1585 (s), 1558 (m), 1482 (s), 1423 (s), 1401 (m).



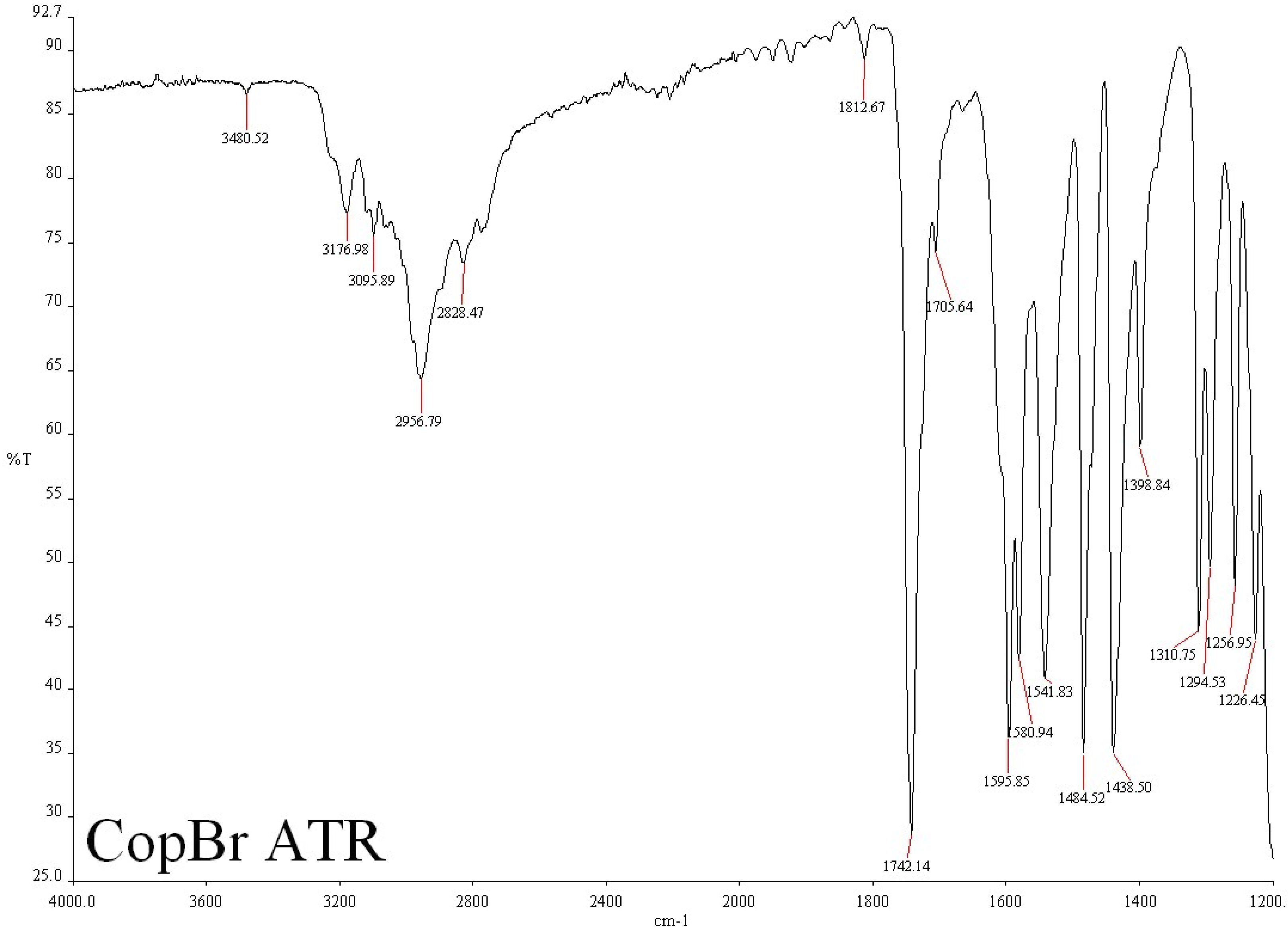
1.3.3.5. **CmmBr**: 3235 (w), 3181 (w), 3094 (w), 3042(w), 2932 (m), 2879 (m), 2814 (m), 1751 (s), 1741 (s), 1614 (m), 1588 (s), 1560 (s), 1471 (s), 1424 (s).



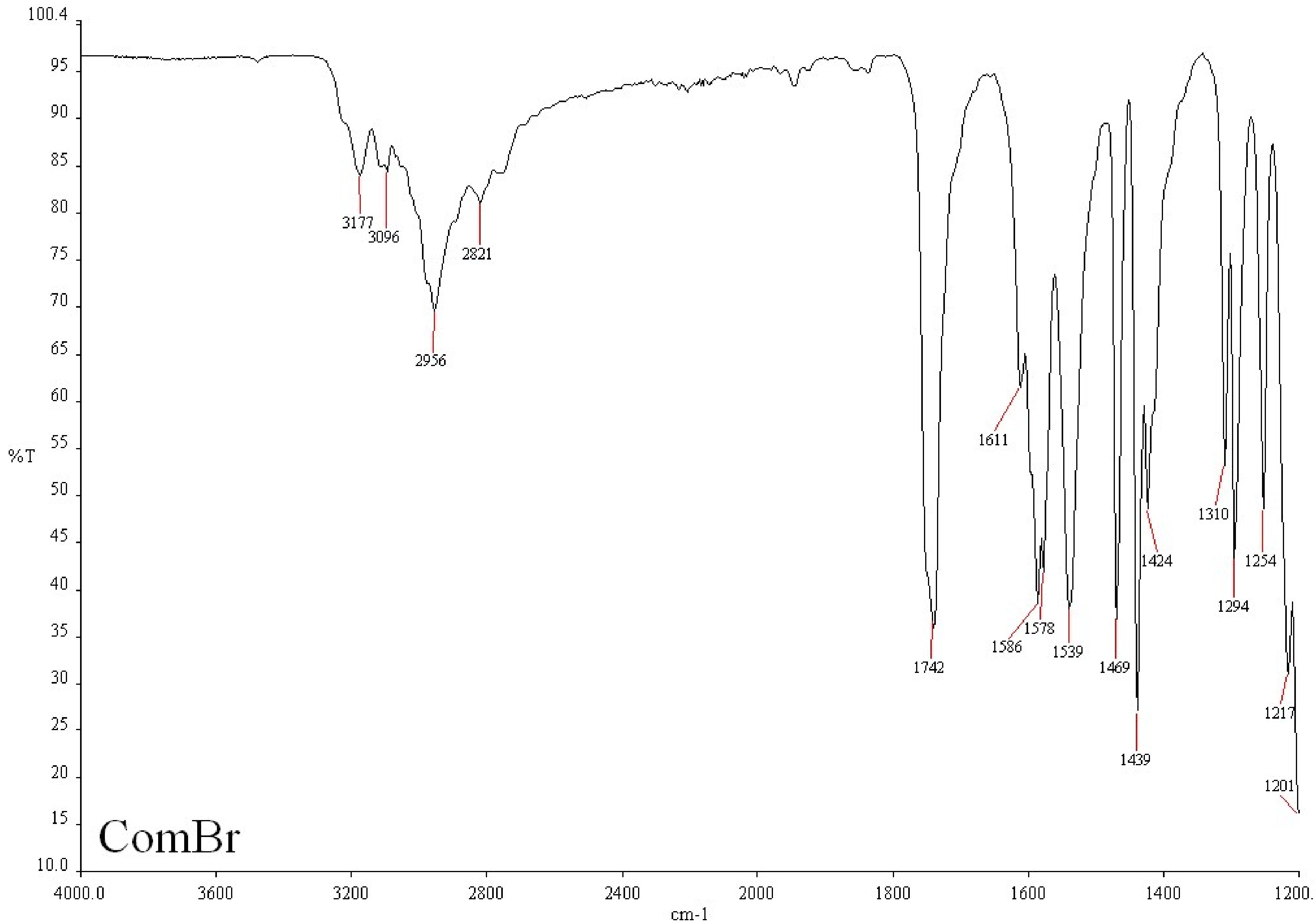
1.3.3.6. **CmoBr**: 3525 (m), 3178 (m), 3042 (m), 2990 (m), 2904 (w), 2842 (w), 1720 (s), 1655 (w), 1611 (m), 1553 (m), 1553 (s), 1484 (m), 1446 (m), 1414 (m).



1.3.3.7. **CopBr**: 3481 (w), 3177 (w), 3096 (w), 2957 (m), 2828 (w), 1742 (s), 1706 (w), 1596 (s), 1581 (s), 1542 (s), 1484 (s), 1438 (s).



1.3.3.8. **ComBr**: 3177 (w), 3096 (w), 2956 (m), 2821 (w), 1742 (s), 1611 (m), 1586 (s), 1578 (s), 1539 (s) 1469 (s), 1439 (s), 1424 (m).



2. Crystal structure data

Pages 109-112 **Full details available from CIF.**

Table 1	**Experimental details of the nine CmpX, CmmX and CopX structures.**
Table 2	**Selected hydrogen-bond parameters (Å, °)**

and

Page 123	**Table 3: Summary of the CxxX isomer grids with selected structural features.**

Table 1. Experimental details

Experiments were undertaken at 294 K using a Xcalibur, Sapphire3, Gemini Ultra; Mo $K\alpha$ radiation for eight structures and **CopBr** using Cu $K\alpha$.

Crystal data_(crystal growth)	**CmpF**_(acetone:$CHCl_3$)	**CmpCl**_(acetone:$CHCl_3$)	**CmpBr**_(acetonitrile)	**CmmF**_($CHCl_3$)
Chemical formula	$C_{12}H_9FN_2O_2$	$C_{12}H_9ClN_2O_2$	$C_{12}H_9BrN_2O_2$	$C_{12}H_9FN_2O_2$
M_r	232.21	248.66	293.12	232.21
Crystal system, space group	Monoclinic, *Pc*	Monoclinic, *Pc*	Monoclinic, *Pc*	Monoclinic, *Cc*
a, *b*, *c* (Å)	12.1578(3), 3.7938(1), 23.0837(6)	12.9792(3), 3.8079(1), 23.0781(6)	13.2502(3), 3.8621(1), 22.9979(8)	26.1331(19), 3.7572(3), 11.9066(7)
α, β, γ (°)	90, 95.103(2), 90	90, 95.036(2), 90	90, 94.861(2), 90	90, 115.765(8), 90
V (Å^3)	1060.50(5)	1136.20(5)	1172.65(6)	1052.85(14)
Z	4	4	4	4
μ (mm^{-1})	0.11	0.33	3.50	0.11
Crystal size (mm)	0.43×0.38×0.10	0.33×0.18×0.08	0.15×0.15×0.05	0.34×0.17×0.11
Data collection				
Absorption correction	Analytical (ABSFAC)	Analytical (ABSFAC)	Analytical (ABSFAC)	Analytical (ABSFAC)
T_{min}, T_{max}	0.959, 0.989	0.921, 0.975	0.577, 0.849	0.970, 0.991
Measured, independent, observed refl	6916, 3554, 3158 {$I>2\sigma(I)$}	7270, 4260, 3727 {$I>2\sigma(I)$}	7123, 3624, 2408 {$I>2\sigma(I)$}	3146, 1683, 1344 {$I>2\sigma(I)$}
R_{int}	0.023	0.035	0.059	0.034
θ_{max}(°)	27.5	27.5	27.2	27.1
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.649	0.642	0.642
Refinement				
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.106, 1.07	0.047, 0.129, 1.11	0.050, 0.090, 1.03	0.053, 0.126, 1.07
No. of reflections	3554	4260	3624	1683
No. of parameters	315	315	315	158
No. of restraints	2	2	2	2
H-atom treatment	Mixed	Mixed	Mixed	Mixed
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.18, -0.14	0.27, -0.23	0.27, -0.30	0.24, -0.17
Absolute structure	Flack x from 917 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack & Wagner, 2013).	Flack x from 1310 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack & Wagner, 2013).	Classical Flack method	Flack x from 357 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack & Wagner, 2013).
Absolute structure parameter	0.2(10)	0.04(7)	0.019(14)	-4.7(10)

Crystal data_(crystal growth)	**CmmCl**_(CHCl$_3$:acetone:toluene)	**CmmBr**_(CHCl$_3$:CH$_3$CN)	**CopF**_(CHCl$_3$:acetone)	**CopCl**_(CHCl$_3$:acetone)	**CopBr**_(THF)
Chemical formula	$C_{12}H_9ClN_2O_2$	$C_{12}H_9BrN_2O_2$	$C_{12}H_9FN_2O_2$	$C_{12}H_9ClN_2O_2$	$C_{12}H_9BrN_2O_2$
M_r	248.66	293.12	232.21	248.66	293.12
Crystal system, space group	Monoclinic, *Ia*	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	12.0058(9), 3.7726(6), 24.477(3)	3.8827(5), 24.756(2), 17.742(2)	3.8471(4), 11.6218(19), 12.467(2)	3.8776(9), 11.481(4), 13.085(5)	11.349(6), 3.9443(16), 26.137(8)
α, β, γ (°)	90, 93.046(11), 90	90, 91.789(14), 90	108.261(15), 90.417(11), 95.461(11)	105.84(3), 90.64(2), 92.82(2)	90, 101.34(5), 90
V (Å^3)	1107.1(2)	1704.5(3)	526.52(14)	559.5(3)	1147.2(9)
Z	4	6	2	2	4
μ (mm^{-1})	0.34	3.61	0.11	0.33	4.83
Crystal size (mm)	0.25×0.16×0.06	0.30×0.11×0.09	0.73×0.06×0.03	0.53×0.05×0.03	0.52×0.07×0.01
Data collection					
Absorption correction	Multi-scan (Empirical)	Multi-scan (Empirical)	Analytical (ABSFAC)	Multi-scan (Empirical)	Multi-scan (Empirical)
T_{min}, T_{max}	0.37, 1.00	0.79, 1.00	0.964, 0.996	0.585, 1.000	0.487, 1.000
Measured, independent, observed refl {I>2σ(I)}	3732, 2059, 1100	10527, 5993, 1546	5561, 1965, 1260	4234, 1972, 930	4128, 1718, 1169
R_{int}	0.046	0.105	0.043	0.082	0.053
θ_{max}(°)	27.8	27.9	26.5	25.2	61.2
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.656	0.659	0.627	0.599	0.568
Refinement					
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.081, 0.233, 1.05	0.052, 0.096, 0.63	0.046, 0.114, 1.02	0.079, 0.224, 1.00	0.070, 0.215, 1.03
No. of reflections	2059	5993	1965	1972	1718
No. of parameters	154	460	158	158	158
No. of restraints	2	39	0	0	0
H-atom treatment	Constrained	Constrained	Mixed	Mixed	Mixed
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.48, -0.27	0.63, -0.65	0.15, -0.14	0.31, -0.26	0.87, -0.39
Absolute structure	Flack x from 311 quotients [(I+)-(I-)]/[(I+)+(I-)]	Classical Flack method.	–	–	–
Absolute structure parameter	0.07 (10)	-0.008 (18)	–	–	–

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET) (compiled Jan 20 2011, 15:58:25), *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS14*/7 (Sheldrick, 2014), *SHELXS2014*/7 (Sheldrick, 2014), *SHELXL97*, *SHELXL14*/7 (Sheldrick, 2008) & SORTX (McArdle, 1995), *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009), *SHELXL14*/7. Absorption correction ABSFAC, Clark and Reid, 1998); Multi-scan (Empirical SCALE3 ABSPACK) H atom treatment: H atoms treated by a mixture of independent and constrained refinement. Flack x determined using ??? quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack & Wagner, *Acta Cryst*. **B69** (2013) 249-259).

Table 2. Selected hydrogen-bond parameters (Å, °)

D—H···*A*	*D*—H (in Å)	H···*A* (in Å)	*D*···*A* (in Å)	*D*—H···*A* (in °)
CmpF				
N1A—H1A···N23B	0.80(3)	2.20(3)	2.999(4)	174(3)
N1B—H1B···N23A^{i}	0.79(4)	2.16(4)	2.941(4)	179(4)
C16A—H16A···O1B^{ii}	0.93	2.30	3.201(4)	164
C16B—H16B···O1A^{iii}	0.93	2.43	3.313(4)	160
C22A—H22A···O1A	0.93	2.26	2.867(4)	122
C22B—H22B···O1B	0.93	2.55	2.933(4)	105
CmpCl				
N1A—H1A···N23B	0.82(4)	2.16(4)	2.980(5)	176(4)
N1B—H1B···N23A^{i}	0.80(4)	2.13(4)	2.929(5)	173(4)
C16A—H16A···O1B^{ii}	0.93	2.29	3.193(5)	163
C16B—H16B···O1A^{iii}	0.93	2.42	3.299(5)	157
C22A—H22A···O1A	0.93	2.28	2.879(5)	122
C22B—H22B···O1B	0.93	2.54	2.929(5)	106
CmpBr				
N1A—H1A···N23B	0.84(8)	2.17(9)	2.985(9)	164(8)
N1B—H1B···N23A^{i}	0.89(7)	2.04(7)	2.927(9)	171(6)
C16A—H16A···O1B^{ii}	0.93	2.30	3.199(9)	163
C16B—H16B···O1A^{iii}	0.93	2.42	3.296(10)	157
C22A—H22A···O1A	0.93	2.27	2.881(9)	122
C22B—H22B···O1B	0.93	2.55	2.934(9)	105
C22B—H22B···O2A	0.93	2.60	3.312(8)	133
CmmF				
N1—H1···N23^{iv}	0.86(7)	2.10(7)	2.950(5)	173(5)
C16—H16···O1^{i}	0.93	2.38	3.254(5)	157
C22—H22···O1	0.93	2.47	2.920(6)	110

CmmCl				
N1—H1···N23^{v}	0.86	2.10	2.948(11)	167
C16—H16···O1^{vi}	0.93	2.35	3.223(12)	155
C22—H22···O1	0.93	2.45	2.913(14)	111
CmmBr				
N1A—H1A···N23B	0.86	2.03	2.88(2)	172
C16A—H16A···O1B^{vii}	0.93	2.41	3.27(2)	154
N1B—H1B···N23C	0.86	2.17	3.02(2)	170
C16B—H16B···O1C^{vii}	0.93	2.28	3.18(2)	163
N1C—H1C···N23A^{viii}	0.86	2.08	2.94(2)	176
C22B—H22B···O1B	0.93	2.32	2.89(2)	119
CopF				
N1—H1···N22^{ix}	0.91(2)	2.08(3)	2.994(3)	175(2)
C23—H23···O2^{ix}	0.93	2.57	3.271(3)	133
C26—H26···O1	0.93	2.28	2.868(3)	121
CopCl				
N1—H1···N22^{ix}	0.86(5)	2.15(5)	3.001(7)	170(4)
C23—H23···O2^{ix}	0.93	2.57	3.267(8)	133
C26—H26···O1	0.93	2.29	2.872(7)	121
C13—H13···O1^{x}	0.93	2.53	3.425(8)	163
CopBr				
N1—H1···N22^{xi}	0.86(8)	2.14(8)	2.975(8)	163(7)
C15—H15···O1^{xii}	0.93	2.40	3.307(9)	165
C23—H23···O2^{xi}	0.93	2.58	3.290(9)	134
C26—H26···O1	0.93	2.26	2.850(9)	121

Symmetry code(s): (*i*) *x*, -*y*+1, *z*-1/2; (*ii*) *x*, *y*-1, *z*; (*iii*) *x*, -*y*+2, *z*-1/2; (*iv*) *x*, -*y*, *z*-1/2; (*v*) *x*+1/2, -*y*+2, *z*; (*vi*) *x*+1/2, -*y*+3, *z*; (*vii*) *x*+1, *y*, *z*; (*viii*) *x*-1, *y*, *z*-1; (*ix*) -*x*+2, -*y*+1, -*z*; (*x*) -*x*+2, -*y*+1, -*z*+1; (*xi*) -*x*+1, -*y*, -*z*+1; (*xii*) -*x*+1/2, *y*-1/2, -*z*+1/2.

3. *Ab initio calculations*

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CxxF	Optimisation results; PES scans of **C-rings** and **F-rings**; PES scans of carbamate backbone
CxxCl	Optimisation results; PES scans of **C-rings** and **Cl-rings**; PES scans of carbamate backbone
CxxBr	Optimisation results; PES scans of **C-rings** and **Br-rings**; PES scans of carbamate backbone

3.1. CxxF isomer grid

3.1.1. CxxF Optimisation results

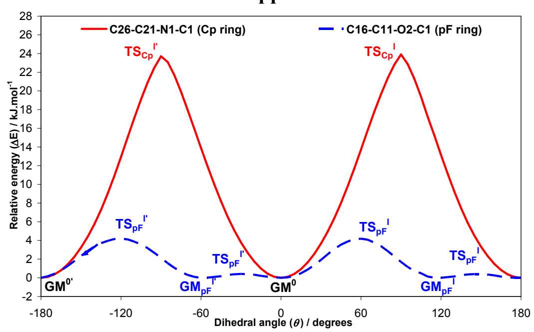
CxxF	$\alpha/°$	$\beta/°$	$\gamma/°$	$\delta/°$
CppF	-0.67	121.00	-0.24	0.21
CpmF	0.10	125.69	-0.80	-0.62
CpoF	-0.03	75.37	6.28	1.00
CmpF	-0.87	121.19	-0.25	-0.05
CmmF	-0.29	56.8	0.89	0.72
CmoF	-1.39	74.54	6.30	1.06
CopF	-0.32	121.65	-0.29	-0.16
ComF	-0.65	56.02	0.82	0.75
CooF	-0.98	74.20	5.56	0.82

Details as in the main body of manuscript.

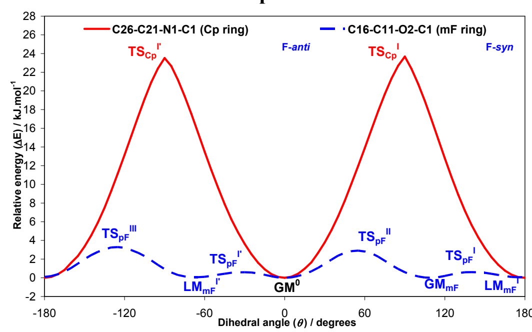
3.1.2. Conformational analysis results

3.1.2.1. Potential energy surface (PES) scans of **C**-rings and **F**-rings in nine **CxxF** conformers (rotamers)

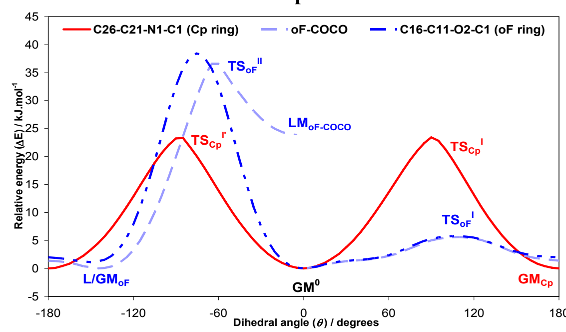
CppF



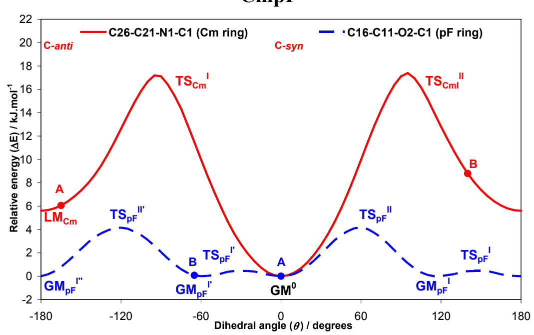
CpmF



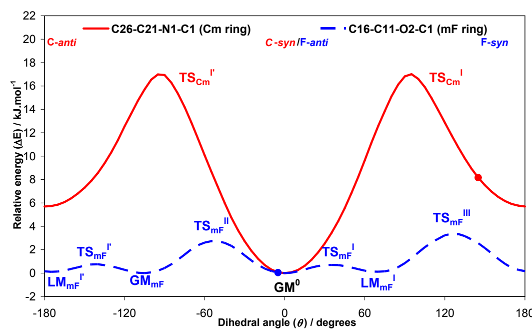
CpoF



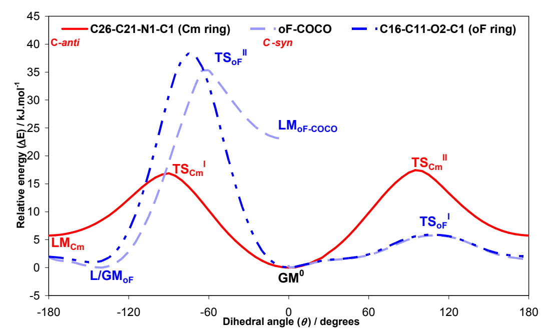
CmpF



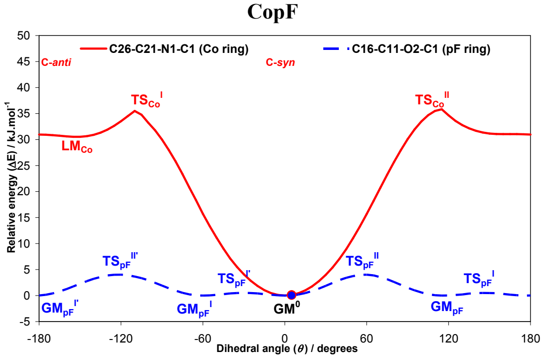
CmmF



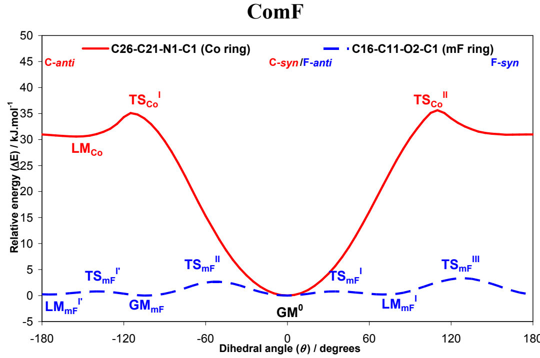
CmoF



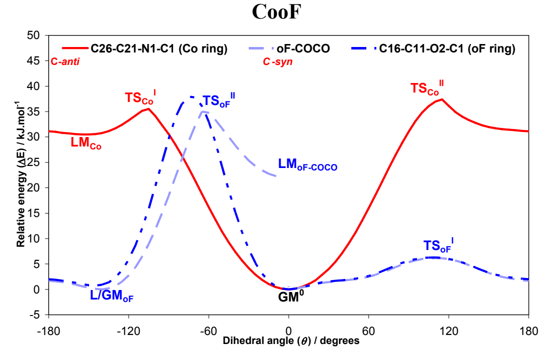
CopF



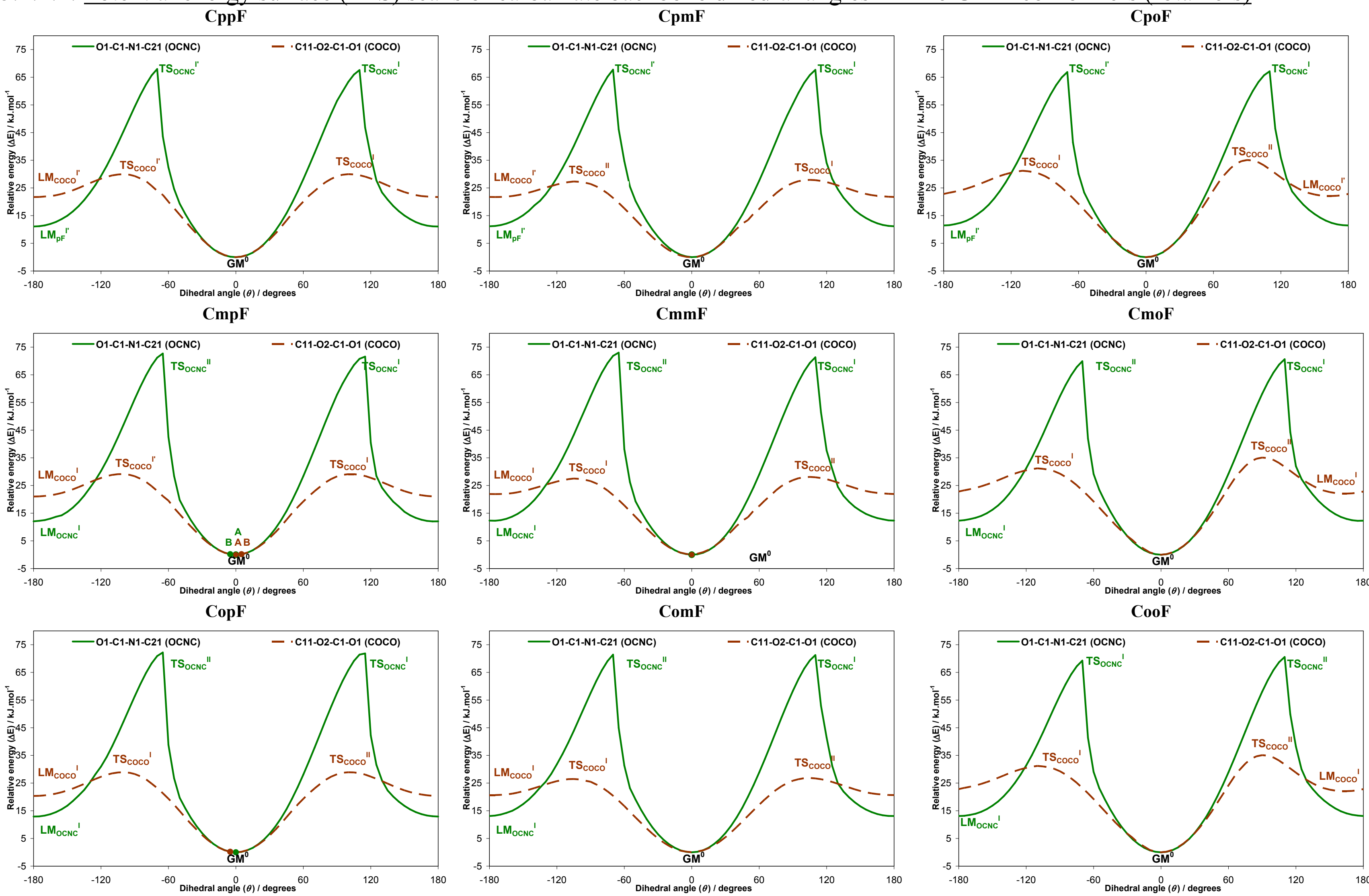
ComF



CooF



3.1.2.2. Potential energy surface (PES) scans of carbamate backbone dihedral angles in nine **CxxF** conformers (rotamers)



3.2. CxxCl isomer grid

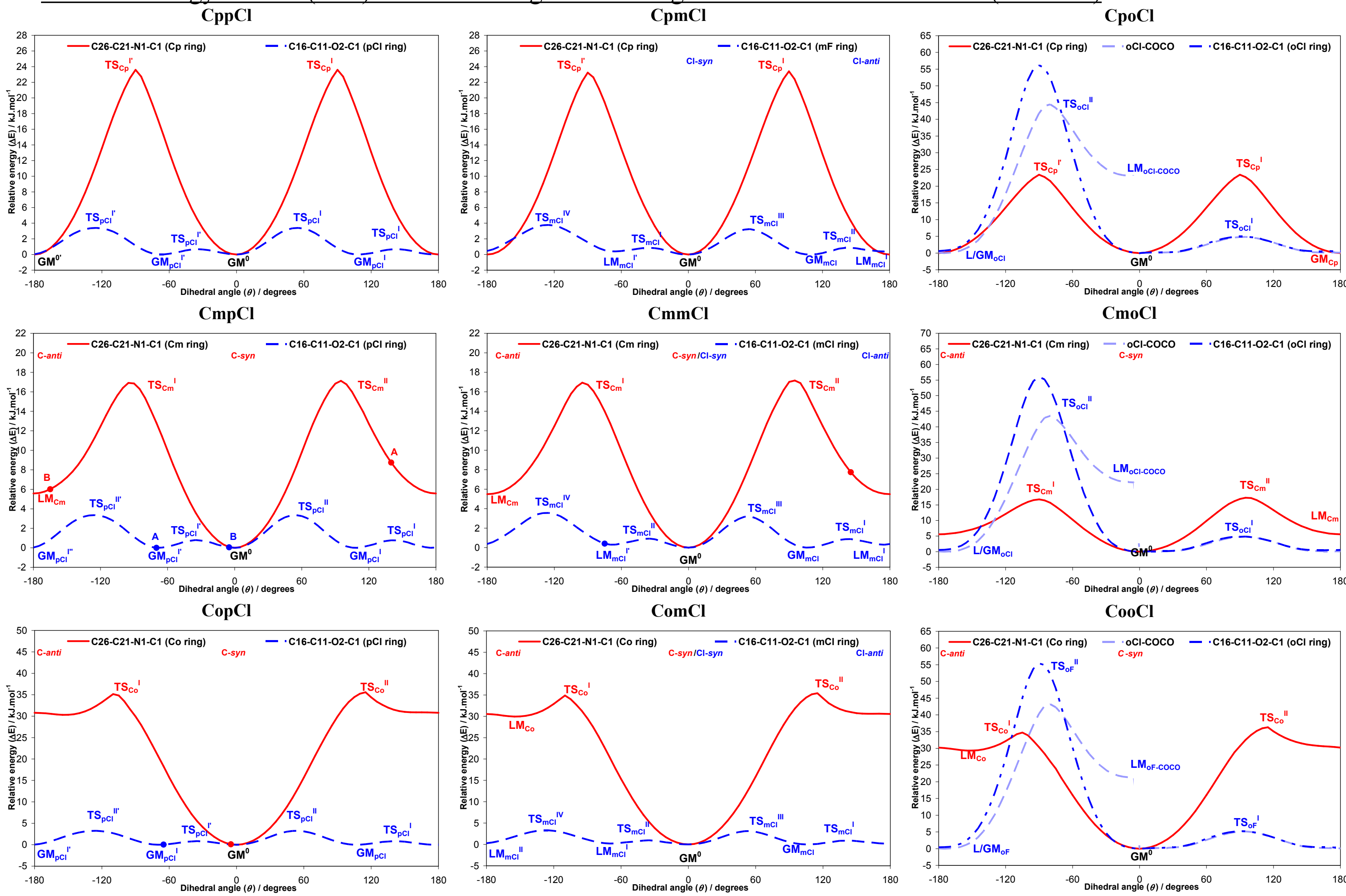
3.2.1. CxxCl Optimisation results

CxxCl	α/°	β/°	γ/°	δ/°
CppCl	-0.76	125.79	-0.85	0.13
CpmCl	-0.38	126.03	-0.82	-0.28
CpoCl	-0.16	90.71	4.96	0.67
CmpCl	-1.09	125.97	-0.88	-0.13
CmmCl	-0.52	126.82	-0.90	-0.32
CmoCl	-0.97	90.59	5.06	0.69
CopCl	-0.35	126.63	-0.88	-0.29
ComCl	0.18	127.09	-0.94	-0.58
CooCl	-0.48	90.41	4.32	0.50

Details as in the main body of manuscript.

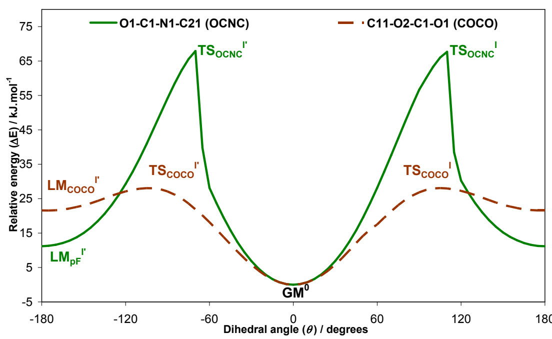
3.2.2. Conformational analysis results

3.2.2.1. Potential energy surface (PES) scans of **C**-rings and **Cl**-rings in nine **CxxCl** conformers (rotamers)

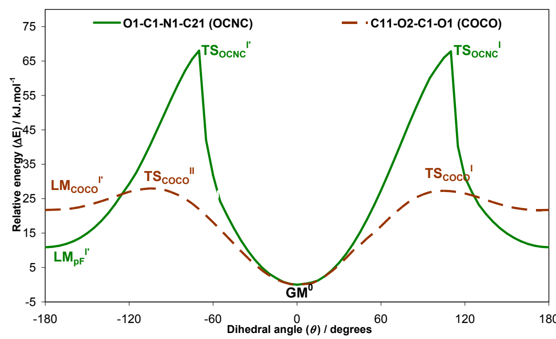


3.2.2.2. Potential energy surface (PES) scans of carbamate backbone dihedral angles in nine **CxxCl** conformers (rotamers)

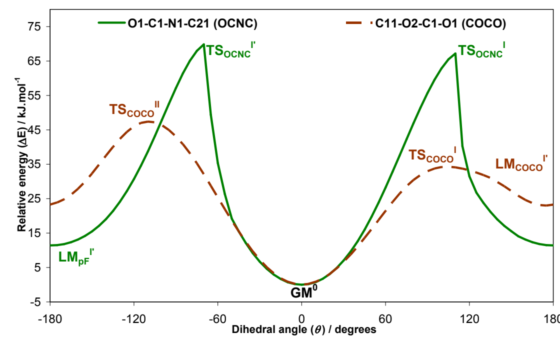
CppCl



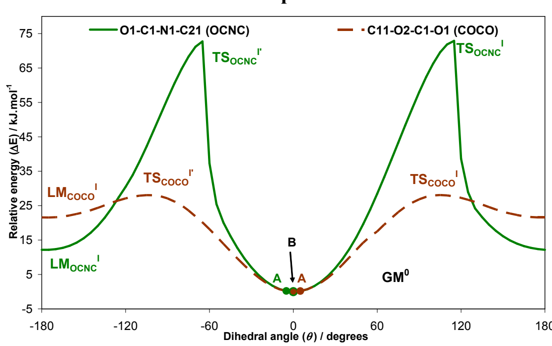
CpmCl



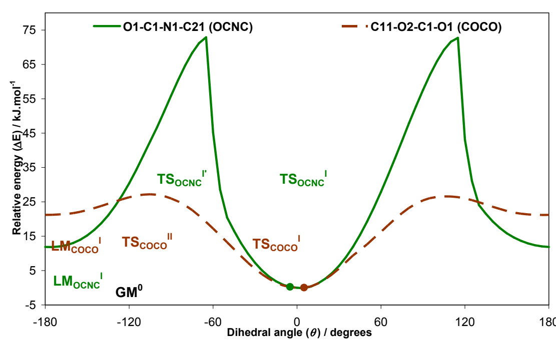
CpoCl



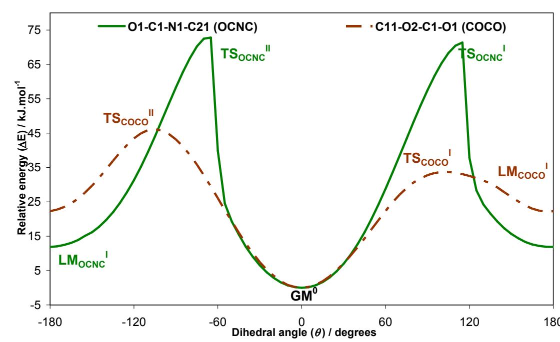
CmpCl



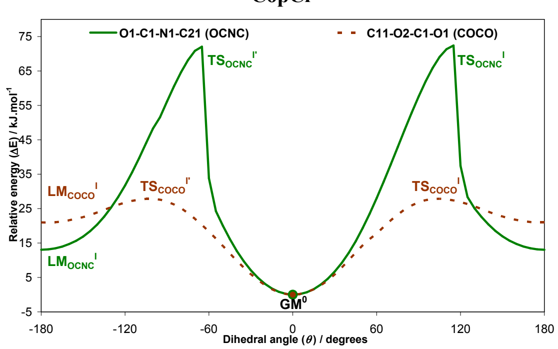
CmmCl



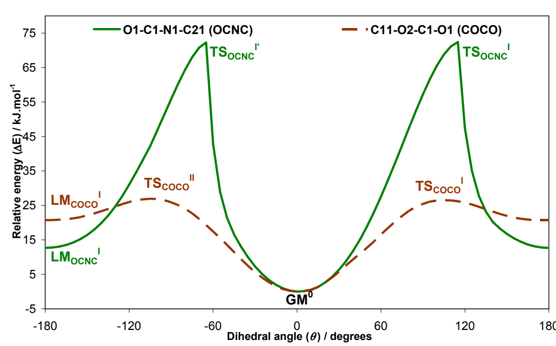
CmoCl



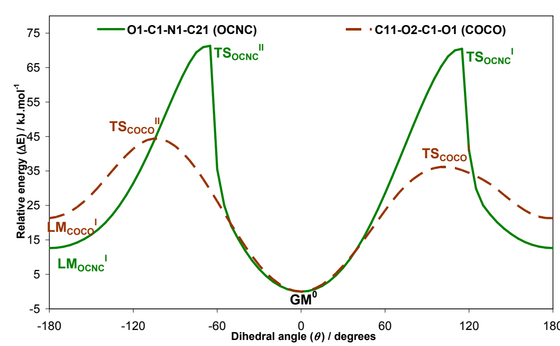
CopCl



ComCl



CooCl



3.3. CxxBr isomer grid

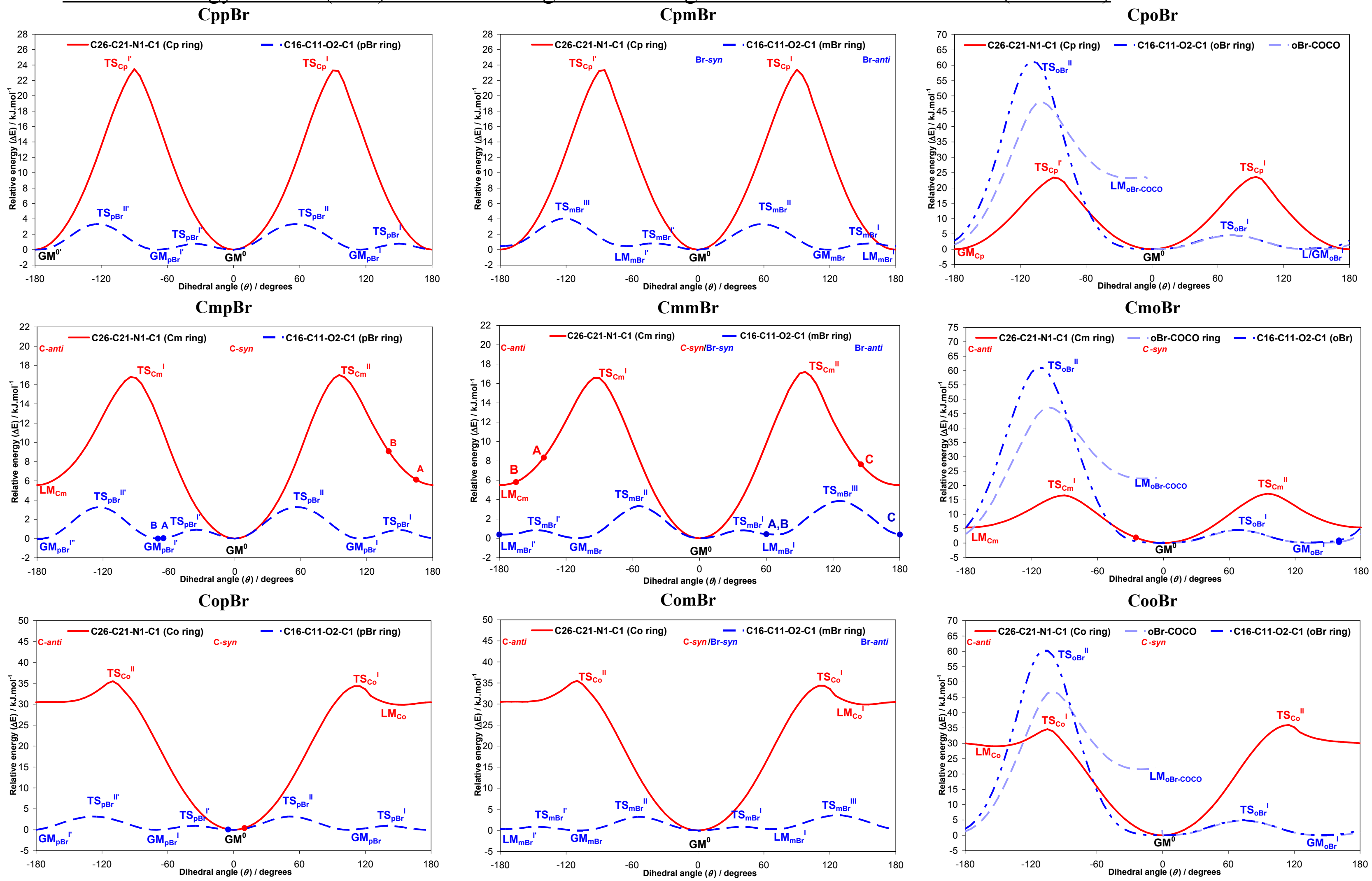
3.3.1. CxxBr Optimisation results

CxxBr	α/°	β/°	γ/°	δ/°
CppBr	-0.75	127.07	-0.92	0.23
CpmBr	-0.43	125.3	-0.75	-0.35
CpoBr	0.38	111.04	2.70	0.15
CmpBr	-1.15	127.34	-1.03	0.00
CmmBr	0.99	57.98	0.89	0.47
CmoBr	-0.29	111.38	2.58	-0.06
CopBr	-0.38	127.93	-0.99	-0.20
ComBr	-0.15	57.06	0.80	0.63
CooBr	0.12	110.21	1.82	-0.30

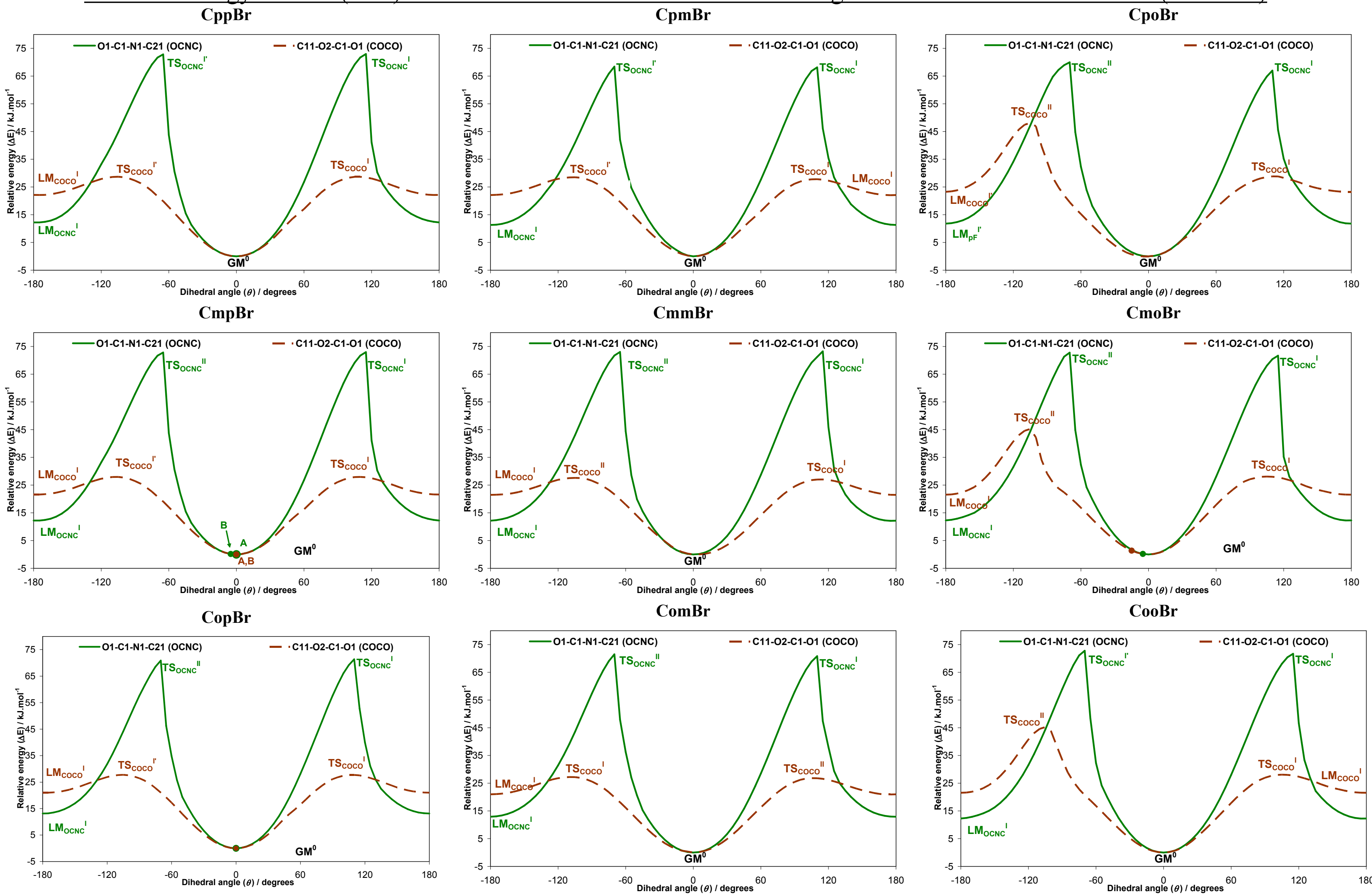
Details as in the main body of manuscript.

3.3.2. Conformational analysis results

3.3.2.1. Potential energy surface (PES) scans of **C**-rings and **Br**-rings in nine **CxxBr** conformers (rotamers)



3.3.2.2. Potential energy surface (PES) scans of carbamate backbone dihedral angles in nine **CxxBr** conformers (rotamers)



Section 4:

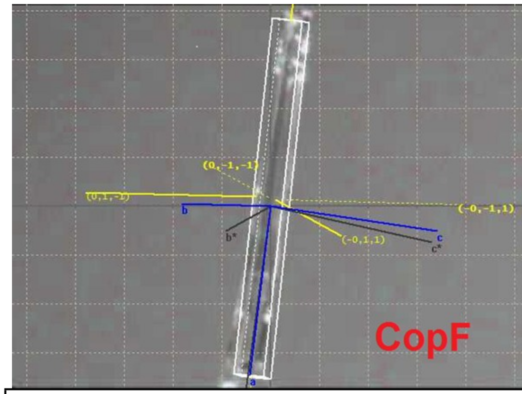
Table 3: Summary of the **CxxX** isomer grids with selected structural features

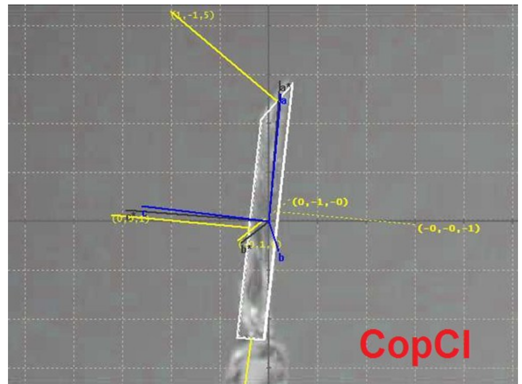
Isomer	Space group	*Z′*	Hydrogen bonding in solid state	Conformation (solid-state)	Conformation (*gas phase*)	Match	Amide H shift /ppm[a]
CppF	-	-	-	-	-	-	7.30
CpmF	-	-	-	-	**F-*anti***	-	8.10
CpoF	-	-	-	-	**-**	-	7.71
CmpF	*Pc*	2	N-H···N	**C-*anti***	**C-*syn***	✘	7.82
CmmF	*Cc*	1	N-H···N	**C-*anti*/F-*anti***	**C-*syn*/F-*anti***	✘	8.10
CmoF	-	-	-	-	**C-*syn***	-	8.26
CopF	*P1*	1	(N-H···N)$_2$*	**C-*syn***	**C-*syn***	✓	9.47
CppCl	-	-	-	-	-	-	7.98
CpmCl	$P2_1$	1	N-H···N	**Cl-*anti***	**Cl-*syn***	✘	7.14
CpoCl	-	-	-	-	-	-	8.04
CmpCl	*Pc*	2	N-H···N	**C-*anti***	**C-*syn***	✘	7.49
CmmCl	*Cc*	1	N-H···N	**C-*anti*/Cl-*anti***	**C-*syn*/Cl-*syn***	✘	7.70
CmoCl	-	-	-	-	**C-*syn***	-	8.40
CopCl	*P1*	1	(N-H···N)$_2$	**C-*syn***	**C-*syn***	✓	9.43
ComCl	-	-	-	-	**C-*syn*/Cl-*syn***	-	9.58
CooCl	-	-	-	-	**C-*syn***	-	10.5
CppBr	-	-	-	**-**	-	**-**	7.09
CpmBr	-	-	-	**-**	**Br-*syn***	**-**	7.27
CpoBr	-	-	-	-	-	**-**	8.22
CmpBr	*Pc*	2	N-H···N	**C-*anti***	**C-*syn***	✘	7.83
CmmBr	$P2_1$	*3*	N-H···N	**C-*anti*/Br-*anti***	**C-*syn*/Br-*syn***	✘	8.08
CmoBr*	$P2_1/c$	1	(N-H···O-H)$_2$	**C-*syn***	**C-*syn***	✓	8.06
CopBr	$P2_1/n$	1	(N-H···N)$_2$	**C-*syn***	**C-*syn***	✓	9.36
ComBr	-	-	-	-	**C-*syn*/Br-*syn***	-	10.0

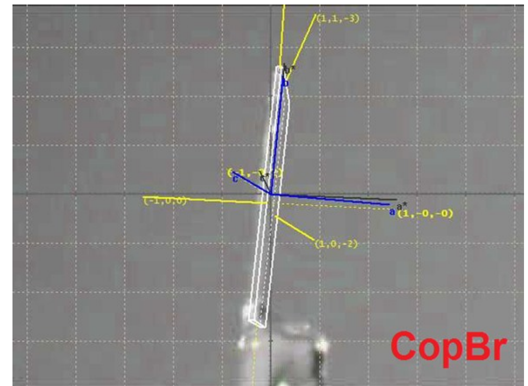
[a] in $CDCl_3$, * monohydrate

Section 5: Examples of Crystal growth for the CopX triad.

The three **CopX** crystal samples serve as examples of needle-like and filamentous growth in the **CxxX** series.







CopF_($CHCl_3$:acetone)	**CopCl**_($CHCl_3$:acetone)	**CopBr**_(THF)
0.73 × 0.06 × 0.03	0.53 × 0.05 × 0.03	0.52 × 0.07 × 0.01

The three **CopX** are representative of the crystal growth characteristics of the **CxxX** series of compounds and crystallise as needles that diffract. At least half of the **CxxX** crystal samples (as grown from a variety of solvent conditions) crystallise as very thin fibres or 'whiskers' that bend very easily and don't diffract on a conventional in-house X-ray diffractometer.

SECTION 6: MELTING POINT ANALYSIS OF CXXX

Melting Point Analysis of CxxX

CxxF	pF	mF	oF	Averages
Cp	184	162	168	171.3
Cm	166	152	135	151
Co	179	/	/	179
	176.3	157	151.5	

CxxCl	pCl	mCl	oCl	
Cp	198	195	169	187.3
Cm	174	170	124	156
Co	199	174	145	172.7
	190.3	179.7	146	

CxxBr	pBr	mBr	oBr	
Cp	206	193	168	189
Cm	169	154	87	136.7
Co	195	175	/	185
	190	174	127.5	

Analysis and trends

	X = F	Cl	Br	Averages	
CpxX	171.3	187.3	189	182.5	Cp
CmxX	151	156	136.7	147.9	Cm
CoxX	179	172.7	185	178.9	Co

<u>CpxX > CoxX > CmxX</u>

For *para-/meta/ortho-* N-pyridine rings

182.5 > 179 > 148°C

	X = F	Cl	Br	Averages	
CxpX	176.3	190.3	190	185.5	pX
CxmX	157	179.7	174	170.2	mX
CxoX	151.5	146	127.5	141.7	oX

<u>CxpX > CxmX > CxoX</u>

For *para-/meta-/ortho-* X-halogenated rings

185.5 > 170 > 142°C